Enhancement of TE polarized light extraction efficiency in nanoscale (AlN)$_m$/GaN$_n$ ($m>n$) superlattice substitution for Al-rich AlGaN disorder alloy: ultra-thin GaN layer modulation

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Abstract

The problem of achieving high light extraction efficiency in Al-rich Al$_x$Ga$_{1-x}$N is of paramount importance for the realization of AlGaN-based deep ultraviolet (DUV) optoelectronic devices. To solve this problem, we investigate the microscopic mechanism of valence band inversion and light polarization, a crucial factor for enhancing light extraction efficiency, in Al-rich Al$_x$Ga$_{1-x}$N alloy using the Heyd–Scuseria–Ernzerhof hybrid functional, local-density approximation with 1/2 occupation, and the Perdew–Burke–Ernzerhof functional, in which the spin–orbit coupling effect is included. We find that the microscopic Ga-atom distribution can effectively modulate the valence band structure of Al-rich Al$_x$Ga$_{1-x}$N. Moreover, we prove that the valence band arrangement in the decreasing order of heavy hole, light hole, and crystal-field split-off hole can be realized by using nanoscale (AlN)$_m$/GaN$_n$ ($m>n$) superlattice (SL) substituting for Al-rich Al$_x$Ga$_{1-x}$N disorder alloy as the active layer of optoelectronic devices due to the ultra-thin GaN layer modulation.
valence band maximum, i.e., the heavy hole band, has $p_x$- and $p_y$-like characteristics and is highly localized in the SL structure, which leads to the desired transverse electric (TE) polarized ($E \perp c$) light emission with improved light extraction efficiency in the DUV spectral region. Some important band-structure parameters and electron/hole effective masses are also given. The physical origin for the valence band inversion and TE polarization in (AlN)$_m$(GaN)$_n$ SL is analyzed in depth.

Keywords: valence band inversion, spin–orbit coupling, electronic structure, optical property, first-principles calculation

1. Introduction

Al$_x$Ga$_{1-x}$N alloys have a large direct band gap from 3.4 eV for GaN to 6.2 eV for AlN, making them very useful for ultraviolet (UV) and deep ultraviolet (DUV) light emitting diodes (LEDs), laser diodes (LDs), and visible/solar-blind UV detectors with operating wavelength down to 200 nm [1–5]. These optoelectronic devices can be widely used in the areas of water purification, bio-agent detection, sterilization, and medicine [6–9]. However, it is still a formidable task to pursue highly efficient DUV LEDs and LDs due to the low light extraction efficiency ($\sim 0.1\%$ at 230 nm) and emission power (a few tens of nW) of the Al-rich Al$_x$Ga$_{1-x}$N active layer in these devices [6]. The key issue in the Al-rich AlGaN-based active region is related to its valence subband crossover (see figure 1 in reference [10]), which is different from that of the InGaN-based active region. In the InGaN-based active region, the charge separation effect is a key limitation on light extraction efficiency. To suppress the charge separation effect induced by the strong built-in electric field (in the magnitude of MV/cm) due to spontaneous and piezoelectric polarization effects [11], several approaches (semipolar-plane growth [12], staggered quantum well (QW) [13, 14], ternary InGaN substrate [15], etc.) have been proposed to improve electron-hole wave function overlap and the radiative recombination rate in InGaN-based LEDs. Recently, some light scattering or redirection structures, such as reflective scattering structures [16], GaN micro-domes [17], colloidal-based microlens arrays [18], TiO$_2$ microsphere arrays [19], and silica sphere arrays [20], have also been adopted to improve light extraction efficiency in these LED devices. The optimized light extraction efficiency based on these novel structures can be expected to be enhanced several times compared with that of conventional planar LEDs.

It has been known that light extraction efficiency has a close relationship to light polarization because it determines the light emission patterns and their propagation direction in Al-rich AlGaN-based LEDs. The intensity of light emission with transverse electric (TE) polarization, originating from the interband optical transition between the conduction and heavy hole (HH) bands, in $c$-oriented Al$_x$Ga$_{1-x}$N decreases dramatically with increasing Al content [17, 21–25]. The transverse magnetic (TM) component of spontaneous emission becomes dominant in Al-rich Al$_x$Ga$_{1-x}$N due to strong interband optical transition from the conduction to the crystal-field split-off hole (CH) band. Obviously, there is a critical Al content, i.e., the cross-point between the HH and CH bands, at which light switches its polarization from TE to TM mode [10]. However, the reported polarization switching values are scattered. For example, Nam et al [21] found that the emitted light alters its polarization from TE to TM mode in
Al$_x$Ga$_{1-x}$N epitaxial layers grown on c-plane sapphire for $x>0.25$. Kawanishi et al [22] reported that the light-polarization switching occurs at $x \approx 0.36$–0.41 in Al$_x$Ga$_{1-x}$N multi-quantum wells (MQWs) on AlN/SiC substrate. The threshold up to $x \approx 0.82$ for light emission with TE polarization in Al$_x$Ga$_{1-x}$N MQW LEDs with well width of $\sim 1.3$ nm has also been observed [26, 27]. The high polarization switching value in the thin QW structures has been attributed to the effect of strain and quantum confinement [26]. It is natural to raise an important question with respect to achieving TE polarization in Al-rich Al$_x$Ga$_{1-x}$N alloy other than in thin QW structures. Our purpose here is to investigate the fundamental physics, explore effective ways to increase the polarization switching value, and enhance TE polarized light extraction efficiency in Al-rich Al$_x$Ga$_{1-x}$N alloy.

The low light extraction efficiency in Al-rich Al$_x$Ga$_{1-x}$N is because of its AlN-like valence band structure and polarization property, which are different from those of GaN [28, 29]. For a wurtzite (WZ) structure, the combined action of crystal-field splitting and spin–orbit coupling (SOC) leads to a three-edge structure at the top of the valence band. A negative crystal-field splitting energy $\Delta_{cr}$ exists in AlN because it has a much smaller $c/a$ ratio and a larger $u$ parameter than those of GaN [29]. Thus, the top three levels of valence band in AlN are $\Gamma_{7v}$ (CH), $\Gamma_{9v}$ (HH), and $\Gamma_{7v}$ light hole (LH), in decreasing order of energy. The superscript (subscript) stands for the corresponding irreducible representation without (with) the SOC effect. Because of the very large negative $\Delta_{cr}$ in AlN ($\Delta_{cr} \approx -220$ meV), the fundamental optical transition at the $\Gamma$ point is from the conduction band to the top CH band. The zone center wave function of the CH band has almost $|Z|$-like character [30]. Hence the light polarization is mainly parallel to the crystal c-axis ($E \parallel c$). On the other hand, the positive crystal-field splitting energy in GaN leads to the sequence of $\Gamma_{9v}$ (HH), $\Gamma_{5v}$ (LH), and $\Gamma_{3v}$ (CH) of the top valence band [28, 31], which gives rise to the fundamental optical transition between the conduction and HH bands. The dominant light polarization thus becomes perpendicular to the c-axis ($E \perp c$) because the wave function of the HH band at the zone center is mainly composed of $|X \pm iY|$ characters [30]. As a consequence, Al-rich AlGaN-based LEDs and LDs show dominant TM
polarization other than the desired TE polarization when Al content exceeds the cross-point between the HH and CH bands [10].

We note that nanometer-scale compositional inhomogeneity has an important influence on the luminescence efficiency of group III nitride semiconductors [32–37]. It has been well accepted that indium atoms form nanometer-scale In-rich quantum dot-like structures in InxGa1−xN alloys due to phase separation [34–36], which significantly enhances light emission efficiency. Recent first-principles calculations also show that several-atom In–N clusters, as radiative recombination centers, can highly localize electrons at the valence band maximum (VBM) and dominate the light emission in Ga-rich InxGa1−xN alloy even though it has a high threading dislocation density (10⁹ cm⁻²) [38–41]. Similarly, it has been proved that the nanoscale islands or quantum dots observed in AlxGa1−xN ternary alloy can improve its internal quantum efficiency [32, 33, 37]. Furthermore, atomic-scale compositional superlattice (SL) has also been observed in Al-rich AlxGa1−xN thin films grown by molecular-beam epitaxy [42–46]. Based on the six-band k·p formalism, Zhang et al found that the TE-polarized optical gain can be enhanced by using the optimized AlGaN-δ-GaN QWs [47, 48]. We thus believe that the nanometer scale compositional inhomogeneity should have a great impact on the electronic structures and optical properties of Al-rich AlxGa1−xN ternary alloy and can enhance its light extraction efficiency. This paper is dedicated to solving the key issues of valence band inversion and light polarization in Al-rich AlxGa1−xN alloy by focusing our attention on the nanoscale compositional inhomogeneity in it. We will investigate the fundamental physics related to valence band crossover and explore possible ways to enhance the TE polarized light extraction efficiency of AlGaN-based DUV LEDs and LDs based on first-principles calculations. To guarantee the reliability of our calculations for the electronic structures and optical properties, we carefully compare our results obtained from three different schemes, i.e., Heyd–Scuseria–Ernzerhof (HSE) [49, 50], local-density approximation with 1/2 occupation (LDA-1/2) [51], and generalized gradient approximation with the Perdew–Burke–Ernzerhof (GGA–PBE) [52] functional. By simulating different Ga-atom distributions in Al-rich AlxGa1−xN ternary alloy, we find that the nanoscale (AlN)ₘ/(GaN)ₙ (ₘ>ₙ) SL with an ultra-thin GaN layer, such as one GaN monolayer, can convert the VBM from the CH to the HH band, which directly leads to TE polarized light emission in the DUV spectral region.

The rest of this paper is organized as follows. In section 2, we outline our calculation methods. The numerical results for the electronic structures and optical properties of (AlN)ₘ/(GaN)ₙ (ₘ>ₙ) SL and Al-rich AlxGa1−xN disorder alloy are given and discussed in section 3. The SOC effect is taken into account to obtain the accurate band structure near the Γ point. Section 3.1 gives the electronic band structures and densities of states (DOSs). In section 3.2, some important band parameters associated with the k·p Hamiltonian are given by means of direct fitting to our first-principles band structures. The electric charge density and optical properties are calculated and discussed in sections 3.3 and 3.4, respectively. The physical origin of valence band inversion in (AlN)ₘ/(GaN)ₙ SL is thoroughly analyzed in section 3.5. Finally, our main conclusions are summarized in section 4.

2. Calculation methods

Our first-principles calculations are based on the density functional theory (DFT) and are carried out using the Vienna ab initio simulation package (VASP) code [53, 54], implemented
with projector augmented wave (PAW) potentials [55]. We adopt the AM05 exchange-correlation (XC) functional [56] to optimize our structural parameters because it can give more reasonable lattice constants than the traditional LDA and GGA–PBE [57, 58]. The important SOC effect is taken into account in the present calculations. The active layer of DUV optoelectronic devices (LEDs and LDs) usually consists of an Al-rich Al\textsubscript{x}Ga\textsubscript{1−x}N MQW with a typical thickness of 20–30 nm [27, 59, 60], which can be constructed from an ~20-period WZ AlGaN supercell (~1.5 nm) generated by 3 × 3 × 3 primitive cells (see figure 1). Two different Ga distributions are considered here. One is nanoscale (AlN)\textsubscript{n}/(GaN)\textsubscript{n} SL, and the other is Al\textsubscript{0.83}Ga\textsubscript{0.17}N disorder alloy (see figures 1(c) and (d)). The Al (3s\textsuperscript{2}3p\textsuperscript{1}), Ga (3d\textsuperscript{10}4s\textsuperscript{2}4p\textsuperscript{1}), and N (2s\textsuperscript{2}2p\textsuperscript{3}) are treated as the valence electrons. A cutoff energy of 550 eV for the plane-wave basis set is used. The Brillouin zone integration is sampled with a 4 × 4 × 2 Γ-centered Monkhorst–Pack [61, 62] \textit{k}-point mesh. Convergence with respect to the plane-wave cutoff energy and \textit{k}-point sampling has been carefully checked. The total energy is converged to less than 10^{-5} eV during the geometry optimization. The forces acting on all atoms are less than 0.02 eV Å\textsuperscript{-1}. The lattice parameters and atomic coordinates are optimized by minimizing the total energy and the Hellmann–Feynmann forces so that the strains caused by the large covalent radius of the Ga atom can be released completely in our SL structures. The optimized structures are then used to calculate the electronic structures and optical properties of Al-rich the Al\textsubscript{x}Ga\textsubscript{1−x}N alloy. Note that our SL structures can be achieved by means of metalorganic vapor phase epitaxy [44], switched atomic layer metalorganic chemical vapor deposition [63], and molecular beam epitaxy [64].

Considering that the band gap in the usual LDA and GGA calculations is seriously underestimated due to an incomplete cancellation of artificial self-interaction and the lack of discontinuity of the exchange-correlation potential in going from the valence to the conduction band, we adopt the LDA-1/2 method [51] and the HSE hybrid functional [49, 50] to improve our calculations. Generally, the LDA-1/2 method includes the self-energy of the particle excitation and can give an accurate band gap of semiconductors at a computational cost comparable to the ordinary LDA or GGA [51]. In the LDA-1/2 scheme, the atomic self-energy potential is expressed as the difference between the all-electron potentials of the atom and those of the half-ion [51, 65], i.e.,

\[
V_s \approx V(0, r) - V(-1/2, r). 
\]

The potential \(V_s\) has a long-range Coulomb tail that has to be trimmed by means of a function

\[
\Theta(r) = \begin{cases} 
1 - \left(\frac{r}{CUT}\right)^n, & (r \leq CUT), \\
0, & (r > CUT).
\end{cases}
\]

In equation (2), the value of \(CUT\) is chosen such that the resulting energy band gap of the crystal reaches its extreme. The values of \(CUT\) and \(n\) are further tested by means of a comparison with experimental band gaps of GaN and AlN. The half ionization is applied to the \(p\)-orbital of the N atom and the \(d\)-orbital of the Ga atom. We adopt \(CUT = 2.90\) (a.u.) and \(n = 8\) for the N atom, and \(1.23\) (a.u.) and \(100\) for the Ga atom. The calculated band gaps with these parameters are 3.51 and 6.09 eV for GaN and AlN, respectively, which are in good agreement with their experimental values. Hence these parameters are also used to calculate the band structures of the Al-rich Al\textsubscript{x}Ga\textsubscript{1−x}N alloy.
Within the HSE scheme, the exchange-correlation functional is constructed through a weighted mixing of the PBE \[52\] exchange ($x$) and correlation ($c$) functional and the Hartree–Fock (HF) exchange term, i.e.,

$$E_{xc}^{\text{HSE}} = \alpha E_{x}^{\text{HF,SR}}(\mu) + (1 - \alpha) E_{x}^{\text{PBE,SR}}(\mu) + E_{x}^{\text{PBE,LR}}(\mu) + E_{c}^{\text{PBE}}, \quad (3)$$

where the exchange interaction is separated into short-range (SR) and long-range (LR) parts, $\mu$ is the screening parameter, and $\alpha$ is the exact exchange mixing ratio. In general, the band-structure parameters and the electron and hole effective masses obtained from the HSE calculation are accurate and reliable, even though the HSE calculation is computationally demanding. Some calculations have indicated that the band gap increases if the exchange mixing ratio $\alpha$ increases in the HSE scheme \[66, 67\]. We find from our HSE calculation that the band gaps of 3.60 eV for GaN and 6.00 eV for AlN can be obtained by choosing $\alpha = 0.32$ and $\mu = 0.20$. These band gap values are very close to the experiments and previous calculations (see table 1). We thus adopt $\alpha = 0.32$ and $\mu = 0.20$ to calculate the electronic structures and optical properties of the Al-rich Al$_{x}$Ga$_{1-x}$N alloy.

In our optical property calculations, we adopt a dense $8 \times 8 \times 4$ $k$-point mesh and a Gaussian smearing width of 0.05 eV. The frequency-dependent dielectric tensor is determined within the random phase approximation. Using the longitudinal expression under the long-wavelength limit, the $\alpha\beta$ ($\alpha, \beta = x, y, z$) component of the imaginary part $\varepsilon_2$ of the dielectric function can be expressed as \[77\].

**Table 1.** Comparison of band gap ($E_g$) and top valence band width (VBW) calculated by using the HSE hybrid functional ($\alpha = 0.32$ and $\mu = 0.20$) with other calculational and experimental results for GaN and AlN.

|        | $E_g$ (eV) | VBW (eV) |
|--------|-----------|----------|
| **GaN** |           |          |
| This work | 3.60      | 7.74     |
| Other calculations | 3.50$^a$ | 8.00$^a$ |
|           | 3.47$^b$ | 7.40$^c$ |
| Experiments | 3.60$^d$ | 7.00$^f$ |
|           | 3.51$^f$ | —        |
| **AIN**  |           |          |
| This work | 6.00      | 6.67     |
| Other calculations | 5.80$^a$ | 6.90$^a$ |
|           | 6.11$^b$ | 6.70$^c$ |
| Experiments | 6.0–6.3$^d$ | —       |
|           | ~6.0$^a$ | —        |

$^a$ GW calculation from reference \[68\].
$^b$ Empirical pseudopotential calculation from reference \[69\].
$^c$ LDA calculation from reference \[68\].
$^d$ Reflectivity measurement; see reference \[70\].
$^e$ Synchrotron radiation photoemission spectroscopy; see reference \[71\].
$^f$ Experimental value at 1.6 K; see reference \[72\].
$^g$ References \[73–76\].
$^h$ Experimental value at 300 K; see reference \[72\].
\[
\epsilon_{2,q}^{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \to 0} \frac{1}{q^2} \sum_{c,v,k} 2w_k \delta(E_{c,k} - E_{v,k} - \hbar \omega) \\
\times \langle u_{c,k+e_{\alpha} q} | u_{v,k} \rangle \langle u_{v,k+e_{\beta} q} | u_{c,k} \rangle^*,
\]

(4)

where \(e_\alpha\) represents the unit vector in the \(\alpha\) direction; \(q\) denotes the wavenumber of the incident electromagnetic wave; \(\Omega\) is the volume of the unit cell; \(c\) and \(v\) refer to conduction and valence band states, respectively; \(w_k\) is the \(k\) point weight which sums to 1; and \(u_{c,k}\) is the cell periodic part of the wavefunctions at the \(k\) point. The real part \(\epsilon_1\) of the dielectric function can be derived from the usual Kramers–Kronig transformation [78]. If we choose the \(c\)-axis of the WZ crystal along the \(z\)-direction of the Cartesian coordinate system, nonzero components of the dielectric tensor merely correspond to the ordinary (\(\epsilon_{xx} = \epsilon_{yy}\), \(E \perp c\)) and the extraordinary (\(\epsilon_{zz}\), \(E \parallel c\)) light polarization. Once we obtain the dielectric function, the absorption coefficient \(\alpha = 2q\kappa\) with \(\kappa = (\epsilon_1^2 + \epsilon_2^2)\) can subsequently be derived easily.

The general \(k\cdot p\) Hamiltonian for the WZ structure is directly applied to the nanoscale (AIN)\(_m\)/(GaN)\(_n\) SL to get its band-structure parameters by fitting the Hamiltonian to our first-principles band structures because the SL has the same hexagonal symmetry in the \(c\)-plane as GaN and AlN [79]. We solved the eigenvalue equation \(\det (H(k) - E(k)I) = 0\) (\(I\) is a \(6 \times 6\) identity matrix) and fitted the eigenvalues to the band structures obtained from first-principles calculations for GaN, AlN, and (AIN)\(_m\)/(GaN)\(_n\) SL. All the parameters are initialized to obtain \(E_i^{(1)}(k, \{\Delta_j\}, \{A_k\})\) \((i = 1–6\) corresponding to the six eigenvalues, \(j = 1–3\), and \(k = 1–7\)). The conjugate gradient algorithm is then used to iterate the values of these parameters until \(\sum_k |E_i^{(m)}(k, \{\Delta_j\}, \{A_k\}) - E_i(k)\|^2\) \((E_i(k)\) is the first-principles eigenvalue\) is minimized at optimized values of \(\Delta_1, \Delta_2, \Delta_3, A_1, A_2, A_3, A_4, A_5, A_6,\) and \(A_7\) (see references [30, 80, 81] for their definitions). Considering that the \(A_7\) term has a close relationship with the SOC effect and can significantly influence band dispersion, we adopt the block diagonalized Hamiltonian, including the \(A_7\) term, to fit our band structures [81, 82].

3. Results and discussion

3.1. Electronic structures

The optimized lattice parameters for GaN, AlN, and Al\(_{0.83}\)Ga\(_{0.17}\)N with two different Ga distributions, i.e., the (AIN)\(_3\)/(GaN)\(_1\) SL and disorder alloy, are shown in table 2. We can see from table 2 that the results obtained from the AM05 XC functional are in excellent agreement with experimental values. This clearly shows that the AM05 XC functional is accurate and reliable.

To certify that a good electronic structure can be obtained from the lattice parameters optimized with the AM05 XC functional, we recalculate the electronic band structures of GaN and AlN (refer to figure 2) and compare them with previous theoretical and experimental results in detail. We can see from figure 2 that the fourfold degenerate \(I_{6v}\) and doubly degenerate \(I_{1v}\) levels become three doubly degenerate \(I_{9v}, I_{7v}\), and \(I_{7v}\) levels because of the combined action of the crystal field (CF) and SOC. Meanwhile, \(I_{1c}\) becomes the doubly degenerate \(I_{7c}\) level. This energy-splitting process is further explained in figure 3. Generally, the crystal-field splitting energy without SOC can be defined as [85]
Figures 2(a) and (b) show the band structures in the vicinity of the $\Gamma$ point without SOC for GaN and AlN, respectively. We can see from figure 2(b) that $\Delta_{cr} = -227$ meV (a negative energy gap).

\[
\Delta_{cr} = E(\Gamma_v) - E(\Gamma_{tv}).
\] (5)
value) for AlN, which is in good agreement with the previous theoretical value of $-219$ meV [29] and the experimental result of $-220 \pm 2$ meV [86]. On the other hand, we obtain $\Delta_{cr} = 40$ meV (a positive value) for GaN (see figure 2(a)), which is in accordance with the experimental value of 9–38 meV in reference [87] and the theoretical value of 34 meV in reference [88]. Figures 2(c) and (d) further show the electronic band structures of GaN and AlN near the $\Gamma$ point, in which the important SOC effect is included. We can see from figure 2(c) that the calculated energy difference between the A and B (C) valence bands is 4.7 (43.1) meV for GaN, which is in good agreement with the calculated results of 6 (43) meV in reference [28]. The corresponding energy splitting is 13 ($-223.5$) meV for AlN (see figure 2(d)). Excellent agreement with the previous calculation value of 13 ($-213$) meV is confirmed again [29]. The calculated valence band width (VBW) is 7.11 eV for GaN, which is also in good agreement with the experimental value of 7.0 eV [71]. The foregoing results clearly show that the calculated electronic structures from the lattice parameters optimized with the AM05 XC functional are reliable and accurate. We thus will calculate the electronic structures and optical properties of the Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys from the structure optimized with the AM05 XC functional.

It is well known that high Ga concentration is required to reverse the valence band order in $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ternary alloy due to the large negative crystal-field splitting energy in AlN. It is thus quite difficult to achieve valence band order inversion in Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloy. In order to explore possible methods to reverse the top valence band order, we calculate the electronic band structures (see figure 4) of Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ternary alloy with different Ga distributions, i.e., $\text{Al}_{15}\text{Ga}_9\text{N}_{54}$ disorder alloy, $(\text{AlN})_9/(\text{GaN})_1$, $(\text{AlN})_9/(\text{GaN})_2$, and $(\text{AlN})_3/(\text{GaN})_3$ SLs. For simplicity, the SOC effect is not included. Figure 4 clearly shows that the microscopic Ga-atom distribution can effectively modulate the electronic band structures of Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ disorder alloy. The desired valence-band arrangement in the decreasing order of $\Gamma_{9v}$, $\Gamma_{7v}$, and $\Gamma_{7v}^1$ (see figures 4(b)–(d)) can indeed be achieved by means of changing the Ga distribution from

![Figure 3. Schematic representation of band splitting at the $\Gamma$ point for GaN, AlN, and nanoscale $(\text{AlN})_m/(\text{GaN})_n$ (m>n) SL. The valence band is split from the original $\Gamma_6$ and $\Gamma_7$ into $\Gamma_{9v}^1$, $\Gamma_{7v}^1$, and $\Gamma_{7v}^1$, and the conduction band is transformed from $\Gamma_1^c$ to $\Gamma_{7c}^1$ because of the combined action of the crystal field (CF) and SOC. The valence band structure of the $(\text{AlN})_m/(\text{GaN})_n$ SL is similar to that of GaN due to strong modulation of the ultrathin GaN layer.](image-url)
The calculated crystal-field splitting energy is 208.6 meV for the (AlN)5/(GaN)1 SL, which is much larger than the value of −153.5 meV for the Al45Ga9N54 disorder alloy. The band gap of the (AlN)5/(GaN)1 SL has a slight decrease compared with that of the disorder alloy. This clearly indicates that the light emission is still in the DUV spectral region (∼237 nm) with the (AlN)5/(GaN)1 SL substituting for the Al45Ga9N54 disorder alloy as the active layer. We further find that the electronic band structures of the (AlN)m/(GaN)n SLs with n = 1–3 (b–d) in the vicinity of the Γ point from the GGA–PBE calculation. Here the band gaps are revised based on the LDA-1/2 calculation and the SOC effect is not included. It is worthwhile to note that the typical character of the VBM state, dominating the interband optical transition, is converted from the CH (C) band of the disorder alloy to the desired HH (A) band of the (AlN)m/(GaN)n SL due to strong modulation of the ultra-thin GaN layer. The HH and LH bands are degenerate at the Γ point for the SL structure, whereas they split into two bands for the disorder structure.

Figure 4. The electronic band structures of the Al45Ga9N54 disorder alloy (a) and (AlN)m/(GaN)n (m+n = 6) SLs with n = 1–3 (b–d) in the vicinity of the Γ point from the GGA–PBE calculation. Here the band gaps are revised based on the LDA-1/2 calculation and the SOC effect is not included. It is worthwhile to note that the typical character of the VBM state, dominating the interband optical transition, is converted from the CH (C) band of the disorder alloy to the desired HH (A) band of the (AlN)m/(GaN)n SL. The HH and LH bands are degenerate at the Γ point for the SL structure, whereas they split into two bands for the disorder structure.

It is interesting to note that the HH and LH bands are degenerate at the Γ point in the SL structure, whereas there is a separation of 9.3 meV between them in the disorder alloy (see figure 4). The physical reason is that the Ga-atom distribution has the same sixfold rotation symmetry in the SL as in the host crystal. To confirm this conclusion, we further calculate the
The electronic band structure of the $\text{Al}_{48}\text{Ga}_{6}\text{N}_{54}$ alloy with two different Ga-atom distributions. One holds the hexagonal symmetry of the Ga distribution and the other does not. Our calculations show that the HH and LH, mainly with $p_x$- and $p_y$-like characters, are split in the structure without hexagonal symmetry. This is caused by the inequivalence of the $x$ and $y$ directions. In contrast, figure 5 indicates that the HH and LH bands are degenerate at the $\Gamma$ point in the structure with hexagonal symmetry of the Ga-atom distribution.

The electronic band structures and corresponding partial densities of states (PDOSs) for the nanoscale $(\text{AlN})_m/(\text{GaN})_n$ SL are presented in figure 6 with three different methods, i.e., HSE, LDA-1/2, and GGA–PBE, in which the SOC effect is considered. For convenience, the top of the valence band at the $\Gamma$ point is set as the reference energy level for these three different calculations. We can see from figure 6(a) that, according to the HSE calculation, the band gap $E_g$ is 5.24 eV, the energy difference between the HH and LH (LH and CH) is 9.1 (216.7) meV, and the VBW is 7.06 eV. Moreover, both the HH and LH bands become flat and dispersionless levels along the $\Gamma$–$A$ direction, which indicates that the HH and LH are highly localized and have a very large effective mass along the $c$-axis (listed in table 4). Figure 6(b) shows that the conduction band minimum (CBM) is mainly determined by the Ga–$4s$ state. In particular, the PDOS has a sharp peak in the vicinity of the VBM, which is dominated by the $2p$ state of N atoms bonded with Ga atoms. This directly proves the strong localization of the HH and LH in the GaN monolayer in the SL structure. The interband optical transition becomes the desired TE polarization ($\mathbf{E} \perp \mathbf{c}$), which is due to the transition between the VBM determined by N atoms bonded with Ga atoms and the CBM dominated by Ga atoms. This clearly indicates that TE polarization can be achieved in the $(\text{AlN})_m/(\text{GaN})_n$ ($m>n$) SL instead of in the Al-rich $\text{Al}_x\text{Ga}_{1-x}\text{N}$ disorder alloy.

Our LDA-1/2 calculation (see figure 6(c)) shows that the band gap $E_g$ is 5.23 eV, the energy difference between the HH and the LH (LH and CH) is 11.7 (199.1) meV, and the VBW is 5.48 eV. The corresponding results for the GGA–PBE calculation (refer to figure 6(e)) are $E_g = 3.48$ eV, $\Delta E_{AB} = 10.7$ meV, $\Delta E_{BC} = 203.7$ meV, and VBW = 6.42 eV. Obviously, the band gap derived from the LDA-1/2 calculation is in excellent agreement with the HSE result. Except for the band gap, the valence band structures obtained from the GGA–PBE calculation are in...
Figure 6. The calculated electronic band structures and the corresponding PDOSs for the nanoscale (AlN)$_5$(GaN)$_1$ SL in the vicinity of the \( \Gamma \) point with three different schemes: HSE (a, b), LDA-1/2 (c, d), and GGA–PBE (e, f). Here the important SOC effect is included. For simplicity, the PDOSs of some typical N, Al, and Ga atoms are given. The number in parentheses behind the element symbol denotes the atom position (see figure 1(c)).
The \( k \cdot p \) method [30] is widely used to calculate the band structures of semiconductors near the band edge. Many band-structure parameters related to the \( k \cdot p \) Hamiltonian have been well established for WZ GaN and AlN [30, 69, 82, 88–91]. Among these parameters, the valence-band effective mass parameters \( A_i \) \((i=1–7)\) determine the band dispersion and \( \Delta_i \) \((i=1–3)\) determine the splitting energy at the \( \Gamma \) point. Usually the corresponding parameters for the ternary compound \( \text{Al}_x\text{Ga}_{1-x}\text{N} \) are obtained by means of the linear interpolation of GaN and AlN values [92, 93]. Generally speaking, the parameters calculated in this way are unreliable. More specifically, it is impossible to obtain the \( k \cdot p \) parameters of the \( (\text{AlN})_n/(\text{GaN})_n \) SL by linear interpolation. A preferable method to determine these important band-structure parameters for the ternary compound is to fit the \( k \cdot p \) Hamiltonian to the first-principles band structures. Our fitted band-structure parameters for the \( (\text{AlN})_n/(\text{GaN})_1 \) SL are presented in table 3. For the sake of comparison, the band-structure parameters for GaN and AlN together with the previous theoretical data are also listed in table 3. It can be seen from table 3 that our calculated band-structure parameters for GaN and AlN are in excellent agreement with the

### Table 3. Comparison of our calculated \( k \cdot p \) parameters with other theoretical results for GaN and AlN. The last row denotes our calculated \( k \cdot p \) parameters of the nanoscale \((\text{AlN})_5/(\text{GaN})_1 \) SL. Here \( \Delta_i \) \((i=1–3)\) is in units of meV, and \( A_i \) \((i=1–6)\) is in units of \( \hbar^2/2m_0 \). The unit of \( A_7 \) is eVÅ.

|       | \( \Delta_1 \) | \( \Delta_2 \) | \( \Delta_3 \) | \( A_1 \) | \( A_2 \) | \( A_3 \) | \( A_4 \) | \( A_5 \) | \( A_6 \) | \( A_7 \) |
|-------|---------------|---------------|---------------|---------|---------|---------|---------|---------|---------|---------|
| GaN   |               |               |               |         |         |         |         |         |         |         |
| This work | 38.0         | 3.20          | 5.56          | -6.01   | -0.59   | 5.55    | -2.08   | -2.17   | -3.01   | 0.210   |
| Reference [81] | 21.1         | 3.61          | 3.61          | -7.21   | -0.44   | 6.68    | -3.46   | -3.40   | -4.90   | 0.094   |
| Reference [89] | 36.0         | 5.00          | 5.90          | -6.40   | -0.50   | 5.90    | -2.55   | -2.56   | -3.06   | 0.204   |
| Reference [90] | 73.0         | 5.40          | 5.40          | -6.27   | -0.96   | 5.70    | -2.84   | -3.18   | -4.96   | <0.270  |
| Reference [94] | 24.0         | 5.40          | 6.80          | -6.40   | -0.80   | 5.93    | -1.96   | -2.23   | -3.02   | 0.350   |
| Reference [95] | 18.2         | 3.90          | 5.40          | -5.98   | -0.58   | 5.44    | -2.46   | -2.53   | -3.31   | 0.030   |
| AlN   |               |               |               |         |         |         |         |         |         |         |
| This work | -223          | 6.30          | 6.87          | -3.84   | -0.26   | 3.56    | -1.25   | -1.37   | -1.26   | 0.048   |
| Reference [82] | -215          | 6.80          | 5.70          | -3.86   | -0.25   | 3.58    | -1.32   | -1.47   | -1.64   | —       |
| Reference [88] | -295          | —             | —             | -3.99   | -0.31   | 3.67    | -1.15   | -1.33   | -1.95   | 0.026   |
| Reference [69] | -128          | —             | —             | -4.79   | -0.55   | 4.37    | -1.51   | -1.73   | -1.82   | 0.134   |
| Reference [94] | -219          | 6.60          | 6.70          | -3.82   | -0.22   | 3.54    | -1.16   | -1.33   | -1.25   | 0       |
| Reference [95] | -245          | 6.20          | 7.50          | -4.05   | -0.28   | 3.71    | -1.71   | -1.90   | -1.05   | 0       |
| SL    | 208.6         | 5.50          | 5.52          | -3.93   | -0.51   | 3.90    | -2.05   | -1.15   | -2.67   | 0.121   |

good accordance with the HSE calculation. In addition, the PDOSs obtained from the LDA-1/2 (see figure 6(d)) and GGA–PBE (see figure 6(f)) are similar to those derived from the HSE calculation (see figure 6(b)). Furthermore, we calculate the crystal-field splitting energy in the case of ignoring the SOC effect in order to have a comprehensive comparison among these three methods. Our calculated values are 221.3 meV for HSE, 203.2 meV for LDA-1/2, and 208.6 meV for GGA–PBE. All the foregoing results clearly show that the combination of the LDA-1/2 and GGA–PBE methods, instead of the computationally expensive HSE calculation, can give a reliable prediction of the electronic structures of semiconductors.
previous published values. Naturally, the predicted $k \cdot p$ parameters for the (AlN)$_5$/(GaN)$_1$ SL structure are reliable and can be used for device simulations.

The electron and hole effective masses are also calculated based on our first-principles band structures. Considering the anisotropy of the WZ structure, we assume a parabolic energy dispersion for the lowest conduction band with different effective masses in and out of the $c$-plane. The electron effective masses are denoted as $m_\perp^e$ and $m_\parallel^e$ for perpendicular and parallel to the $c$-axis, respectively. The electronic band structure near the CBM is given by the following formula,

$$E(k) = E_0 + c \frac{m_0^2}{m_\perp^e} k_\perp^2 + c \frac{m_0}{m_\parallel^e} \left( k_x^2 + k_y^2 \right),$$

where the factor $\hbar^2/2m_0$ has been merged into the coefficient ($c$). The hole effective mass is modeled by the $k \cdot p$ Hamiltonian [30, 80–82]. The obtained effective masses for the Al$_{0.83}$Ga$_{0.17}$N disorder alloy and the (AlN)$_5$/(GaN)$_1$ SL are shown in table 4. For purposes of comparison, the calculated effective masses for GaN and AlN along with some other theoretical and experimental values are also given. We can see from table 4 that our calculated values for GaN and AlN are in good agreement with other calculations and experiments except for the value of the HH effective mass $m_{\parallel}^{HH}$ for AlN. It is more interesting to point out that both the HH and LH have a very large effective mass ($\sim 33m_0$) along the $\Gamma$–A direction for the (AlN)$_5$/(GaN)$_1$ SL. This clearly shows that the HH and LH are highly localized in the proximity of the VBM, which is useful for improving the light extraction efficiency of Al-rich AlGaN-based LEDs and LDs.

3.3. Charge density of (AlN)$_5$/(GaN)$_1$ superlattice and Al$_{0.83}$Ga$_{0.17}$N disorder alloy

To illustrate the different charge distributions at the $\Gamma$ point for the CBM, HH, LH, and CH bands in the (AlN)$_5$/(GaN)$_1$ SL and the Al$_{0.83}$Ga$_{0.17}$N disorder alloy, we show the corresponding electron charge density in figure 7. The up panel, i.e., figures 7(a)–(d), corresponds to the (AlN)$_5$/(GaN)$_1$ SL; and the down panel, i.e., figures 7(e)–(h), is for the Al$_{0.83}$Ga$_{0.17}$N disorder alloy. We can see from figure 7 that the CBM, HH, and LH states are localized around the GaN monolayer, especially for the HH and LH states. On the other hand, the CBM, CH, HH, and LH bands are delocalized Bloch-like states in the disorder alloy. Both the HH and LH bands are the $p_x$- and $p_y$-like states, whereas the CH band is the $p_z$-like state. The interband optical transition from the CBM to the VBM (CH) becomes $E_{\parallel}c$ (TM polarization) for the disorder alloy due to the $p_z$-like symmetry of the CH state. Nevertheless, the strong $E_{\perp}c$ (TE polarization) optical transition from the CBM to the VBM (HH) can be realized in the (AlN)$_5$/(GaN)$_1$ SL due to the strong localization of the $p_z$- and $p_y$-like HH state. This is suitable for applications of some DUV optoelectronic devices such as LEDs and LDs.

3.4. Optical property of nanoscale (AlN)$_5$/(GaN)$_1$ superlattice

To have a comprehensive understanding of the polarization properties of the (AlN)$_5$/(GaN)$_1$ SL, we further calculate the dielectric spectra and absorption coefficient as a function of the incident photon energy with the HSE, LDA-1/2, and GGA–PBE methods (see figure 8). We can see from figure 8 that the results derived from the HSE and GGA–PBE calculations are similar. At the same time, the dielectric spectra obtained from the LDA-1/2 calculation are in good accordance with the HSE result when the energy is less than 8.0 eV. However, there are some
minor differences for the higher-energy interband optical transition between them due to lacking enough precision for the conduction and valence band structures away from the band edge in the LDA-1/2 calculation. Obviously, the HSE calculation not only corrects the well-known band gap underestimation problem inherent in the GGA–PBE calculation, but can also provide accurate electronic structures as well as optical properties. Moreover, we can see from figure 8 that the peak value of $\varepsilon_{2xx}^2$ and $\varepsilon_{2yy}^2$ at the fundamental absorption edge (black line in figure 8) is larger than that of $\varepsilon_{2zz}^2$ (red line in figure 8). This indicates that the interband optical transition is dominated by the TE polarization in the (AlN)$_5$(GaN)$_1$ SL. This is further confirmed by the absorption spectra (see the insets of figure 8).

Table 4. The effective masses of electron (e), HH, LH, and CH (in units of $m_0$) derived from first-principles band structures, including the SOC effect for GaN, AlN, and Al$_{0.83}$Ga$_{0.17}$N with two different Ga distributions, i.e., nanoscale (AlN)$_5$(GaN)$_1$ SL and disorder alloy. For purposes of comparison, the results from other calculations and experiments are also presented for GaN and AlN.

|          | $m_e^\parallel$ | $m_e^\perp$ | $m_{\text{HH}}^\parallel$ | $m_{\text{HH}}^\perp$ | $m_{\text{LH}}^\parallel$ | $m_{\text{LH}}^\perp$ | $m_{\text{CH}}^\parallel$ | $m_{\text{CH}}^\perp$ |
|----------|-----------------|-------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| **GaN**  |                 |             |                          |                          |                          |                          |                          |                          |
| This work| 0.17            | 0.18        | 1.92                     | 1.49                     | 1.22                     | 0.31                     | 0.17                     | 1.38                     |
| Other calculations | 0.14$^a$        | 0.15$^b$    | 2.20$^h$                 | 1.20$^c$                 | 1.10$^d$                 | 0.15$^d$                 | 0.15$^d$                 | 1.10$^d$                 |
|          | 0.20$^d$        | 0.18$^d$    | 2.00$^a$                 | 1.65$^d$                 | 1.96$^e$                 | 0.18$^f$                 | 0.16$^f$                 | 0.57$^a$                 |
|          | 0.20$^g$        | 0.22$^g$    | 1.85$^g$                 | 1.96$^g$                 | 1.85$^g$                 | 0.18$^g$                 | 0.17$^g$                 | 0.36$^g$                 |
| Experiments | 0.20$^h$        | 0.15–0.23$^b$ | 1.10$^h$                 | 1.60$^b$                 | 1.10$^h$                 | 0.30$^h$                 | 0.15$^h$                 | 1.10$^h$                 |
|          | 0.24–0.29$^i$   | 0.204$^j$   | —                        | —                        | —                        | —                        | —                        | —                        |
| **AlN**  |                 |             |                          |                          |                          |                          |                          |                          |
| This work| 0.30            | 0.31        | 3.67                     | 2.36                     | 3.59                     | 0.34                     | 0.25                     | 3.57                     |
| Other calculations | 0.38$^b$        | 0.39$^b$    | 3.68$^d$                 | 2.18$^c$                 | 3.68$^d$                 | 0.25$^d$                 | 0.25$^d$                 | 3.68$^d$                 |
|          | 0.33$^d$        | 0.25$^d$    | 3.53$^f$                 | 3.05$^g$                 | 3.53$^f$                 | 0.33$^f$                 | 0.26$^f$                 | 4.05$^f$                 |
|          | 0.32$^g$        | 0.31$^g$    | 2.94$^g$                 | 11.11$^g$                | 2.94$^g$                 | 0.26$^g$                 | 0.25$^g$                 | 3.57$^g$                 |
| Experiments | 0.231–0.35$^k$  | 0.242–0.25$^h$ | 3.53$^h$                 | 10.42$^h$                | 3.53$^h$                 | 0.24$^h$                 | 0.25$^h$                 | 3.81$^h$                 |
|          | 0.29–0.45$^l$   | 0.29–0.45$^h$ | —                        | —                        | —                        | —                        | —                        | —                        |
| **Al$_{0.83}$Ga$_{0.17}$N** |                 |             |                          |                          |                          |                          |                          |                          |
| SL       | 0.30            | 0.27        | 32.7                     | 0.70                     | 32.7                     | 0.27                     | 0.22                     | 1.93                     |
| Disorder | 0.26            | 0.28        | 3.23                     | 0.96                     | 4.03                     | 0.36                     | 0.23                     | 2.34                     |

* Empirical pseudopotential calculation from reference [69].
* The G$_0$W$_0$ approximation combined with the DFT calculation from reference [88].
* FP–LMTO calculation with the quasicubic approximation from reference [82].
* FLAPW band structure calculation from reference [90].
* Empirical pseudopotential calculation from reference [96].
* FP–LMTO calculation without the SOC effect from reference 82].
* Quasiparticle self-consistent GW calculations from reference [95].
* Experimental value at 300 K from reference [72].
* Plasma Faraday rotation measurements in n-type GaN from reference [97].
* Polarization-dependent photoluminescence measurements from reference [98].
* Low-temperature near-bandedge cathodoluminescence experiment from reference [99].
3.5. Physical origin of band inversion

It has been known that the crystal-field splitting energy $\Delta_{cr}$ has a sensitive dependence on the cell-internal structural parameter $u$ and the ratio $c/a$ of the lattice constants [28, 29, 100]. Furthermore, it is confirmed that $\Delta_{cr}$ linearly depends on $u$ and $c/a$ in the WZ structure [85]. However, it is still unclear why $\Delta_{cr}$ is positive in GaN and negative in AlN even though the WZ GaN has the same space group $C_{6v}$ as AlN. To have a thorough understanding of the physical origin, we calculate $\Delta_{cr}$ as a function of $c/a$ and $u$ for GaN and AlN (see figures 9 and 10). In our calculations, the $a$-lattice constant is fixed at the experimental value of 3.180 and 3.112 Å for GaN and AlN, respectively. The internal parameter $u$ is fixed to the ideal value of 0.375 when $\Delta_{cr}$ is calculated as a function of $c/a$. We adopt the ideal value $c/a = \sqrt{8/3}$ to calculate $\Delta_{cr}$ as a function of $u$. It can be seen from figures 9 and 10 that $\Delta_{cr}$ has a good linear relationship with $c/a$ and $u$. By virtue of a linear fitting with the following formula [85],

$$
\Delta_{cr} = \Delta_{cr}^0 + \alpha(u - 0.375) + \beta (c/a - \sqrt{8/3}),
$$

we obtain the coefficient $\alpha = -16.3$ eV and $\beta = 1.8$ eV for GaN, whereas $\alpha = -23.5$ eV and $\beta = 3.0$ eV for AlN. In equation (7), $\Delta_{cr}^0$ denotes the crystal-field splitting energy of the ideal WZ structure. Our calculations show that $\Delta_{cr}^0$ is 76.4 meV for GaN and 33.3 meV for AlN.
Figure 8. Dielectric function and absorption coefficient (see insets) of the (AlN)$_5$/GaN SL. Here (a) is the result for HSE, (b) for LDA-1/2, and (c) for the GGA–PBE calculation. The onset E$_0$ of $\epsilon^{xx}_2$ ($= \epsilon^{yy}_2$) is attributed to the band-edge transition $\Gamma^{1\downarrow}_c \rightarrow \Gamma^{7\downarrow}_v$. Based on the LDA-1/2 calculation, the band gap is revised to 5.23 eV in (c) and its inset by using the scissor operator value of 1.75 eV.
It is worthwhile to note that the nanoscale (AlN)$_5$(GaN)$_1$ SL can be regarded as an AlN $3 \times 3 \times 3$ supercell with one layer of Al atoms replaced by Ga atoms. This will lead to an increase in $c/a$ owing to the larger covalent radius of the Ga atom and the decrease in $u$ due to the competition between bond-bending and bond-stretching forces in the (AlN)$_5$(GaN)$_1$ SL [101]. Our calculations (see figures 9 and 10) definitely show that the crystal-field splitting energy is directly proportional to $c/a$ and inversely proportional to $u$. By comparison, the internal structure parameter $u$ has a more profound influence on $\Delta_{cr}$ than $c/a$. We can see from figures 9 and 10 that $\Delta_{cr}$ increases by $\sim 20$ meV if $u$ decreases by 0.001, whereas the increase in $c/a$ by 0.001 leads to an increase in $\Delta_{cr}$ by only $\sim 3$ meV. Considering that both $u$ and $c/a$ are closely related to the bond lengths and bond angles, we thus turn our attention to the relationship of the bond lengths and bond angles to the crystal-field splitting energy in order to explore the physical origin of the valence band inversion in the (AlN)$_m$(GaN)$_n$ SL.

To investigate the influence of bond lengths and bond angles on the crystal-field splitting energy, we present the cation-centered tetrahedron in figure 11, in which $R_1$ denotes the nearest neighbor cation-N bond length along the $c$-axis, $R_2$ is the length of the other three equivalent cation-N bonds, and $\alpha_1$ and $\alpha_2$ are the corresponding bond angles around the cation site. The bond angles, i.e., $\alpha_1$ and $\alpha_2$, are not independent due to the hexagonal symmetry of the WZ

![Figure 9](image_url). Crystal-field splitting energy as a function of (a) $c/a$ and (b) the cell-internal structural parameter $u$ for GaN. The intersection with $\Delta_{cr} = 0$ is denoted as $(c/a)_0$ in (a) and $(u)_0$ in (b).
structure, and $\alpha_2$ can be determined by $\cos \alpha_2 = \left[ 2 - 3 \sin^2 (180^\circ - \alpha_1) \right] / 2$. For the binary alloy, the cell-internal structural parameter $u$ can be exactly expressed as

$$u = \frac{R_1}{2 \left[ R_1 + R_2 \sin (\alpha_1 - 90^\circ) \right]}.$$  

(8)
According to equation (8), we obtain $u = 0.370$ (0.374) for the Al-center (Ga-center) tetrahedron in the (AlN)$_5$/(GaN)$_1$ SL. Compared with the value of $u$ in AlN, $u$ decreases by approximately 0.012, which gives rise to an increase of $\sim 240$ meV in the crystal-field splitting energy. Moreover, $u$ decreases by $\sim 0.003$ of the Ga-center tetrahedron in the (AlN)$_5$/(GaN)$_1$ SL compared with the GaN. This enlarges the positive splitting of crystal field energy by $\sim 60$ meV. We thus can understand that the decreasing order of the CH and HH bands in the Al-rich Al$_x$Ga$_{1-x}$N disorder alloy can be inverted to HH/LH and CH bands in the (AlN)$_5$/(GaN)$_1$ SL.

4. Conclusions

In this paper, we theoretically prove that the valence band order can be inverted and the TE polarized light extraction efficiency can be enhanced in nanoscale (AlN)$_m$/(GaN)$_n$ ($m>n$) SL with an ultra-thin GaN layer instead of in Al-rich Al$_x$Ga$_{1-x}$N disorder alloy by using three different approaches, i.e., HSE, LDA-1/2, and GGA–PBE, in which the SOC effect is included. The calculated electronic band structures from the lattice constants optimized with the AM05 XC functional are in excellent agreement with experiments for GaN and AlN. Our calculations show that the microscopic Ga-atom distribution in the Al-rich Al$_x$Ga$_{1-x}$N alloy can effectively modulate its electronic band structures. The valence-band arrangement in the order HH, LH, and CH from the top can be achieved in the (AlN)$_m$/(GaN)$_n$ SL. The crystal-field splitting energy in the SL is much larger than that in the corresponding disorder alloy. In addition, both HH and LH bands have a very large effective mass ($\sim 33m_0$) in the (AlN)$_m$/(GaN)$_n$ SL. The HH and LH bands are degenerate at the $\Gamma$ point if the Ga-atom distribution holds the hexagonal symmetry. Furthermore, the VBM of the SL structure is the HH band with $p_z$- and $p_y$-like characters, whereas the $p_z$-like CH band becomes the VBM of the disorder alloy. High light extraction efficiency with TE polarization ($E \perp c$) can thus be obtained in the (AlN)$_m$/(GaN)$_n$ SL as opposed to TM polarization in the Al-rich Al$_x$Ga$_{1-x}$N disorder alloy. Our calculations further show that the crystal-field splitting energy is mainly determined by the cell-internal structure parameter $u$, whereas $u$ sensitively depends on the bond lengths and bond angles. It is the variation of bond lengths and bond angles that leads to the inversion of CH and HH bands in the (AlN)$_m$/(GaN)$_n$ SL. We also find from our calculations that the computationally expensive HSE calculation for the electronic structures and optical properties can be substituted by the combination of the GGA–PBE and LDA-1/2 methods. The results obtained in this paper are vital for enhancing the TE polarized light extraction efficiency of Al-rich AlGaN-based DUV LEDs and LDs.

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