When group-III nitrides go infrared: New properties and perspectives
by J. Wu
**When group-III nitrides go infrared: New properties and perspectives**

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Wide-band-gap GaN and Ga-rich InGaN alloys, with energy gaps covering the blue and near-ultraviolet parts of the electromagnetic spectrum, are one group of the dominant materials for solid state lighting and lasing technologies and consequently, have been studied very well. Much less effort has been devoted to InN and In-rich InGaN alloys. A major breakthrough in 2002, stemming from much improved quality of InN films grown using molecular beam epitaxy, resulted in the bandgap of InN being revised from 1.9 eV to a much narrower value of 0.64 eV. This finding triggered a worldwide research thrust into the area of narrow-band-gap group-III nitrides. The low value of the InN bandgap provides a basis for a consistent description of the electronic structure of InGaN and InAlN alloys with all compositions. It extends the fundamental bandgap of the group III-nitride alloy system over a wider spectral region, ranging from the near infrared at ~1.9 μm (0.64 eV for InN) to the ultraviolet at ~0.36 μm (3.4 eV for GaN) or 0.2 μm (6.2 eV for AlN). The continuous range of bandgap energies now spans the near infrared, raising the possibility of new applications for group-III nitrides. In this article we present a detailed review of the physical properties of InN and related group III-nitride semiconductors. The electronic structure, carrier dynamics, optical transitions, defect physics, doping disparity, surface effects, and phonon structure will be discussed in the context of the InN bandgap re-evaluation. We will then describe the progress, perspectives, and challenges in the developments of new electronic and optoelectronic devices based on InGaN alloys. Advances in characterization and understanding of InN and InGaN nanostructures will also be reviewed in comparison to their thin film counterparts. © 2009 American Institute of Physics. [DOI: 10.1063/1.3155798]

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thus been heavily focused on Ga-rich InGaN and GaAlN alloys, whose bandgaps cover the blue and near-ultraviolet parts of the electromagnetic spectrum. Since then, the rapid development of solid state lighting technology has revolutionized the fields of optoelectronics and optics. Figure 1(a) shows the widely adopted International Commission on Illumination chromaticity diagram that relates the color of light to human eye response. As seen in this diagram, InGaN plays a dominant role in the fields covering from the blue to the green, corresponding to 400–530 nm in wavelength, or 3.1 to 2.3 eV in photon energy. The In molar fraction in these materials is limited to <∼0.3. At higher In contents the external quantum efficiency (EQE) of LEDs rapidly drops to an unacceptable level, an effect widely known as the “green valley of death” [Fig. 1(b)].

On the other hand, much less effort has been devoted to InN and In-rich alloys. Earlier InN samples were synthesized using radio-frequency sputtering. In most cases, this or similar methods produced polycrystalline samples with high free electron concentrations (>10¹⁹ cm⁻³) (Ref. 7) and significant oxygen contamination. Such materials typically showed relatively low electron mobilities in the range of 10–100 cm²/V s. The optical absorption measured in these samples showed a strong absorption band in the infrared and an absorption edge at about 1.9 eV. The absorption band was attributed to impurity and free carrier absorption, and the value of 1.9 eV was thus widely quoted as the bandgap of intrinsic InN. One of the unexplained characteristics, however, was the lack of light emission at or near the purported band edge. This was in stark contrast to GaN and Ga-rich InGaN, which show a strong luminescence despite very large concentrations of point and extended defects typical for these materials.

Since then, the quality of nitride films has improved drastically with the availability of InGaN and InAlN films grown by metal-organic chemical vapor deposition (MOCVD). Correspondingly, a tremendous amount of effort has been put into the optical characterization of these films. The increased quality has translated to lower free carrier concentrations associated with unintentional doping, allowing the fundamental optical properties to be deconvoluted from band-filling dominated characteristics. Unexpectedly, it was discovered that the bandgaps of InGaN decrease very rapidly with increasing In content, and fall well below 2 eV for compositions approaching an In fraction of 0.5. The rapid reduction of the bandgap versus the In molar fraction was attributed to a unusually large bandgap bowing parameter.

The major breakthrough came about as a result of improved quality of InN films grown using molecular beam epitaxy (MBE). Growth of thick InN films with much reduced free electron concentrations (<10¹⁸ cm⁻³) and high electron mobilities (>2000 cm²/V s) was essential to the progress in understanding the properties of this material. The room-temperature fundamental bandgap of this type of high-quality InN was measured to be near 1.5 and 1.1 eV, 0.77 eV, 0.7–1.0 eV, 0.7 eV, and finally converged to 0.64 eV.

In this paper we review studies of In-rich group III-nitride alloys in the context of this discovery. It is shown that the newly discovered low value of the energy gap of InN provides a basis for a consistent description of the electronic structure of InN as well as the InGaN and InAlN alloys over the entire composition range. It is the aim of this review to present an up-to-date summary of physical parameters of group III-nitride semiconductors and their alloys. In Sec. II we discuss the narrow bandgap of InN and its related physical properties. This is followed by Sec. III with focus on properties of group III-nitride alloys and Sec. IV on their applications. Finally in Sec. V we summarize recent results obtained with group III-nitride nanostructures. This review is focused on wurtzite-structured nitrides, but zincblende nitrides will also be discussed. Topics not covered in this review are the growth, processing and structural properties of group-III nitrides. We refer interested readers to Refs. 22 and 23 for these topics.

II. NARROW BANDGAP OF InN

A. Optical properties

InN is more difficult to grow than GaN due to its low dissociation temperature (~630 °C) and high equilibrium vapor pressure of nitrogen. Nevertheless, in recent years considerable progress has been made in growth of high-quality wurtzite InN films by MBE (Refs. 14–16) and MOCVD. Under ambient conditions group-III nitrides crystallize in the thermodynamically stable hexagonal wurtzite phase with the space group P6₃mc (C₃ᵥ). MBE growth of InN in cubic zincblende structure with the space group F4₃m (T₄) has also been reported. At a hydrostatic pressure of ~12 GPa, InN undergoes a first-order structural phase transition from the wurtzite into the rocksalt structure with the space group Fm3m (O₃). Figure 2 shows the optical characteristics of a high-quality wurtzite InN film grown by Lu et al. using migration-enhanced MBE and measured by Wu et al.. The free electron concentration is 3.5 × 10¹⁷ cm⁻³ and the electron mobility is 2050 cm²/V s for the film. The optical absorption curve shows a strong onset slightly below 0.7 eV. The optical absorption coefficient rapidly increases to ~10⁶ cm⁻¹ above the onset, typical absorption intensity for direct bandgap semiconductors. There is no bandgap feature in the 1.8–2.0 eV region, i.e., in the energy range of previ-
FIG. 2. (Color online) Absorption and photoluminescence of a high-quality, intrinsic InN film measured at 12 K. The solid line through the absorption data points is a sigmoidal fit. Reference 21.

FIG. 3. (Color online) Absorption (a) and PL (b, log scale) spectra of InN measured at a wide range of temperatures. Panel (c) shows the temperature dependence of the PL peak and the bandgap determined from the absorption curves. The solid curve shows a fit to the bandgap with the standard Varshni’s equation. Reference 21.
TABLE I. Recommended values of basic physical parameters of wurtzite InN, AlN, and GaN. Values not referenced were calculated from commonly accepted parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant $a$ ($T=300$ K) (nm)</td>
<td>0.3112$^a$</td>
<td>0.3189$^a$</td>
<td>0.3533$^a$</td>
</tr>
<tr>
<td>Thermal expansion $d \ln a/dT$ (10$^{-6}$/K)</td>
<td>4.2$^a$</td>
<td>5.6$^a$</td>
<td>3.8$^a$</td>
</tr>
<tr>
<td>Lattice constant $c$ ($T=300$ K) (nm)</td>
<td>0.4982$^a$</td>
<td>0.5185$^a$</td>
<td>0.5693$^a$</td>
</tr>
<tr>
<td>Thermal expansion $d \ln c/dT$ (10$^{-6}$/K)</td>
<td>5.3$^a$</td>
<td>3.2$^a$</td>
<td>2.9$^a$</td>
</tr>
<tr>
<td>Density ($g/cm^3$)</td>
<td>3.23$^a$</td>
<td>6.15$^a$</td>
<td>6.81$^a$</td>
</tr>
<tr>
<td>Phillips ionicity</td>
<td>0.449$^b$</td>
<td>0.500$^b$</td>
<td>0.578$^b$</td>
</tr>
<tr>
<td>Debye temperature (K)</td>
<td>1150$^i$</td>
<td>600$^i$</td>
<td>660$^i$</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>3487$^i$</td>
<td>2791$^i$</td>
<td>2146$^i$</td>
</tr>
<tr>
<td>Decomposition temperature ($^\circ$C)</td>
<td>1040$^i$</td>
<td>850$^i$</td>
<td>630$^i$</td>
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<tr>
<td>Decomposition activation energy (kJ/mol)</td>
<td>414$^i$</td>
<td>379$^i$</td>
<td>336$^i$</td>
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<tr>
<td>Static dielectric constant, $e_x/e_0$</td>
<td>8.5$^a$</td>
<td>8.9$^a$</td>
<td>10.4$^a$</td>
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<tr>
<td>High-frequency dielectric constant, $e_{c,0}$</td>
<td>4.6$^a$</td>
<td>5.4$^a$</td>
<td>6.7$^a$</td>
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<tr>
<td>Bandgap $E_g$ ($T=0$) (eV)</td>
<td>6.25$^f$</td>
<td>3.51$^f$</td>
<td>0.69$^f$</td>
</tr>
<tr>
<td>Bandgap $E_g$ ($T=300$ K) (eV)</td>
<td>6.14$^f$</td>
<td>3.43$^f$</td>
<td>0.64$^f$</td>
</tr>
<tr>
<td>Vashni parameter $\alpha$ (meV/K)</td>
<td>1.799$^f$</td>
<td>0.909$^f$</td>
<td>0.414$^f$</td>
</tr>
<tr>
<td>Vashni parameter $\beta$ (K)</td>
<td>1462$^f$</td>
<td>830$^f$</td>
<td>454$^f$</td>
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<tr>
<td>Electron Effective mass at band edge $m^*_e/m_0$</td>
<td>0.32$^f$</td>
<td>0.20$^f$</td>
<td>0.07$^h$</td>
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<td>Exciton binding energy (meV)</td>
<td>60</td>
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<td>Exciton Bohr radius (nm)</td>
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<td>2.4</td>
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<td>Mg acceptor binding energy (eV)</td>
<td>0.51$^i$</td>
<td>0.17$^i$</td>
<td>0.06$^i$</td>
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<td>Critical point $A_1$ (ev), $U_1\rightarrow U_3$</td>
<td>6.36$^i$</td>
<td>4.88$^i$</td>
<td></td>
</tr>
<tr>
<td>Critical point $E_1$ (eV), $L_{2,4}\rightarrow L_{1,3}$, $M_4\rightarrow M_{1,3}$</td>
<td>7.97$^i$</td>
<td>7.00$^i$</td>
<td>5.35$^i$</td>
</tr>
<tr>
<td>Critical point $E_2$ (eV), $H_1\rightarrow H_1$, $M_2\rightarrow M_1$</td>
<td>8.95$^i$</td>
<td>7.96$^i$</td>
<td>6.05$^i$</td>
</tr>
<tr>
<td>Critical point $E_3$ (eV), $K_{3,3}\rightarrow K_2$</td>
<td>9.25$^i$</td>
<td>7.87$^i$</td>
<td></td>
</tr>
<tr>
<td>$A_1$ (TO) phonon (1/cm)</td>
<td>611$^i$</td>
<td>532$^i$</td>
<td>447$^i$</td>
</tr>
<tr>
<td>$A_1$ (LO) phonon (1/cm)</td>
<td>890$^i$</td>
<td>734$^i$</td>
<td>586$^i$</td>
</tr>
<tr>
<td>$E_1$ (LO) phonon (1/cm)</td>
<td>912$^i$</td>
<td>741$^i$</td>
<td>593$^i$</td>
</tr>
<tr>
<td>$E_1$ (TO) phonon (1/cm)</td>
<td>671$^i$</td>
<td>559$^i$</td>
<td>476$^i$</td>
</tr>
<tr>
<td>$E_1^\parallel$ phonon (1/cm)</td>
<td>657$^i$</td>
<td>568$^i$</td>
<td>488$^i$</td>
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<tr>
<td>$E_1^\perp$ phonon (1/cm)</td>
<td>249$^i$</td>
<td>144$^i$</td>
<td>87$^i$</td>
</tr>
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</table>

$^a$Reference 35.
$^b$Reference 36.
$^c$Reference 37.
$^d$Reference 38.
$^e$Reference 39.
$^f$Reference 40.
$^g$Reference 21.
$^h$Reference 20.
$^i$Reference 41.
$^j$Reference 42.
$^k$References 43–46.
$^l$Reference 47.

behaved optical anisotropy is an indication of the interband nature of the optical transitions near 0.64 eV. The PL peak energy of both the $a$-plane$^{52}$ and the $c$-plane$^{49}$ films exhibits a blueshift with increasing excitation power, which can be attributed to the increasing population of the conduction and valence bands by photocarriers at more intense excitation power.

B. Band structure

1. $k \cdot p$ calculations of conduction band

A direct consequence of the narrow gap of InN is the strong nonparabolicity of the lowest conduction band. It is well known that for narrow direct-gap semiconductors such as InSb and InAs,$^{53}$ the dispersion at the bottom of the conduction band takes a nonparabolic form as a result of the $k \cdot p$ repulsion across the narrow gap between the conduction and valence bands. The problem can be treated analytically using an $8 \times 8$ $k \cdot p$ Hamilton matrix that describes the electron wave functions of the $p$-like valence bands and the $s$-like conduction band.$^{54}$

The spin-orbit splitting $\Delta_{so}$ in a compound semiconductor is comparable to the atomic spin-orbit splitting of its anion valence electrons, which is typically small for light atoms.$^{54}$ Group-III nitrides thus have extremely small $\Delta_{so}$ (<room-temperature $k_BT$), as listed in Table II. Neglecting $\Delta_{so}$ and the spin degree of freedom, the $8 \times 8$ $k \cdot p$ Hamilton matrix reduces to a $4 \times 4$ one. Choosing the electronic wave functions $|\psi\rangle$, $|X+iY/\sqrt{2}\rangle$, $|X-iY/\sqrt{2}\rangle$, and $|Z\rangle$ as the basis, the matrix is written as$^{55}$
We further neglect the crystal-field splitting where $P_{xy}$ and $P_z$ are the momentum matrix elements defining the $k \cdot p$ interaction,

\begin{align}
\begin{align}
H &= \frac{\hbar^2 k^2}{2m_0} + \begin{pmatrix}
E_g + \Delta_{ct} & iP_{xy} k_y & iP_{xy} k_x \\
-iP_{xy} k_y & \Delta_{ct} & 0 \\
-iP_{xy} k_x & 0 & \Delta_{cr}
\end{pmatrix} + H_{\text{remote}}, \tag{2}
\end{align}
\end{align}

where $H_{\text{remote}}$ describes the influence from remote bands, and $P_{xy}$ and $P_z$ are the momentum matrix elements defining the $k \cdot p$ interaction,

\begin{align}
\begin{align}
P_{xy} &= \frac{\hbar}{2m_0} \langle S \rangle \frac{\hbar}{i} \partial_k |X\rangle = \frac{\hbar}{2m_0} \langle S \rangle \frac{\hbar}{i} \partial_k |Y\rangle; \tag{3a}
\end{align}
\end{align}

\begin{align}
\begin{align}
P_z &= \frac{\hbar}{2m_0} \langle S \rangle \frac{\hbar}{i} \partial_k |Z\rangle. \tag{3b}
\end{align}
\end{align}

We further neglect the crystal-field splitting $\Delta_{ct}$ (\textlessthan} 40 meV for InN) and $H_{\text{remote}}$ (remote bands are at least 4 eV away), and assume an isotropic band structure at small $k$ so that $P_{xy} \approx P_z$. With these simplifications the Hamiltonian in Eq. (2) can be diagonalized with the following eigenvalue obtained for the conduction band dispersion:\textsuperscript{20}

\begin{align}
E_C(k) &= E_g + \frac{\hbar^2 k^2}{2m_0} + \frac{1}{2} \left( \sqrt{E_{g}^2 + 4E_P \cdot \frac{\hbar^2 k^2}{2m_0} - E_g} \right). \tag{4}
\end{align}

Here $E_g = 0.64$ eV is the intrinsic bandgap, $m_0$ is the electron mass in vacuum, and $E_P = (2m_0/\hbar^2)|P_0|^2$ is the $k \cdot p$ interaction energy. $E_C(k)$ is referenced to the valence band maximum.

As shown in Eq. (4), the nonparabolicity of the conduction band is more pronounced for small $E_g$ (i.e., narrow-gap semiconductors) or large $E_P$, because the conduction band feels stronger perturbation from the valence bands when $E_g$ is smaller or $E_P$ is larger. At very small $k$ values (i.e., near the $\Gamma$ point), Eq. (4) is simplified into a parabolic band,

\begin{align}
E_C(k) &= E_g + \frac{\hbar^2 k^2}{2m_0^*(0)}, \tag{5}
\end{align}

where the effective electron mass at the $\Gamma$-point conduction band minimum is

\begin{align}
\frac{m_0^*(0)}{m_0} = \left(1 + \frac{E_P}{E_g}\right)^{-1}. \tag{6}
\end{align}

Figure 6 shows the calculated conduction and valence band dispersion using Eq. (4) (nonparabolic) and Eq. (5) (parabolic), respectively. The parabolic dispersion deviates severely from the nonparabolic one when $k > \sim 0.05$ Å, or, as shown below, when the electron concentration $n > \sim 10^{19}$ cm$^{-3}$ so that the Fermi level ($E_F$) is displaced deep into the conduction band.

In the case of degenerate doping, optical absorption is forbidden for transitions below the Fermi surface. Therefore, the onset of the optical absorption would overestimate the intrinsic bandgap, leading to an effect known as the Burstein–Moss effect.\textsuperscript{65} Optical emission below the Fermi surface, such as PL, would be still possible but significantly broadened compared to the intrinsic band edge emission, as illustrated schematically in Fig. 6.\textsuperscript{20} This implies that for heavily doped semiconductors, such as earlier, sputter-grown InN films, the absorption and luminescence spectra should be interpreted with caution.\textsuperscript{66}

The Burstein–Moss shift illustrated in Fig. 6 well explains the discrepancy between the earlier 1.9 eV and the newly established 0.64 eV bandgap. High-quality InN films have been grown by MBE where the free electron concentration is varied over several orders of magnitude by controlled Si doping.\textsuperscript{65} The absorption edge was determined from optical absorption experiments as a function of free electron concentration. The absorption edge, or sometimes referred to as the “optical bandgap,” varies continuously from 0.64 eV, the intrinsic bandgap of InN, to $\sim 2$ eV for samples with $n > 5 \times 10^{20}$ cm$^{-3}$.\textsuperscript{63} Bandgaps of earlier, sputter-grown InN films fall accurately onto this dependence, and are therefore well explained by the Burstein–Moss effect. The high free electron concentrations originate from unintentional dopants such as oxygen and native defects.
Electron concentrations as high as $2 \times 10^{21}$ cm$^{-3}$ have been reported in InN. The extreme $n$-type propensity of InN is a direct consequence of its large electron affinity, as will be discussed in Sec. III B.

The increase in absorption edge with increasing electron concentration was calculated by the dispersion relation in Eq. (4) (nonparabolic) or Eq. (5) (parabolic) evaluated at the Fermi wavevector $k_F = (3 \pi n)^{1/3}$, neglecting the thermal broadening of the Fermi distribution. In the calculation, the conduction band renormalization effects due to electron-electron interaction and electron-ionized impurity interaction are also taken into account. The calculated dependences are compared to the experimental data and to each other in Fig. 7. The calculated optical bandgap assuming a parabolic conduction band shows a Burstein–Moss shift too fast to describe the experimental data.

The conduction band nonparabolicity results in a $k$-dependent electron effective mass given by

$$m^*_e(k) = \frac{\hbar^2}{dE_C(k)/dk}.$$  \hfill (7)

As $k$ approaches 0, Eq. (7) gives the band minimum effective mass defined in Eq. (6). The electron effective mass of InN has been measured by several groups using various methods such as plasma reflection spectroscopy and infrared spectroscopic ellipsometry. Values of $m^*_e(0)/m_0$ at 0.039–0.047, 0.033, 0.14, 0.085, 0.05, and 0.07 and 0.24 have been reported. In the case of plasma reflection spectroscopy, infrared reflection curves are measured and fitted with a standard dielectric function model,

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2,$$  \hfill (8)

where the complex dielectric function is given by the classical dielectric function,
The reflection curves drop rapidly at the plasma frequency \( \omega_p \) given by

\[
\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0\varepsilon_r m_e^*}}.
\]  

Here \( \gamma \) is the damping parameter related to carrier scattering which broadens the plasma reflection edge. The plasma edge shifts to higher energy as \( n \) is increased. The effective mass thus obtained is shown in Fig. 8 together with the values reported by different groups, and compared with calculated results of Eq. (7). It can be seen that although the data were measured by different groups for InN films grown by different methods, the calculations based on the nonparabolic dispersion using different \( E_g \) values show a good agreement with all the measured values. Note that the same value of \( E_P = 10 \) eV was also used in calculating the Burstein–Moss shift in Fig. 7. Therefore, a good consistent picture is established in describing the conduction band of InN based on the \( \mathbf{k} \cdot \mathbf{p} \) model. The extrapolation of the curve in Fig. 8 leads to a small effective mass of \( m_e^*(0)/m_0 = 0.07 \pm 0.02 \) at the bottom of the conduction band. This value agrees very well with recently calculated value between 0.065 and 0.068, \(^{55} \) as will be discussed below. For other values, such as a smaller \( m_e^*(0)/m_0 = 0.05 \) reported by Fu et al., \(^{34} \) a larger \( E_P = 15 \) eV would be needed to fit with it. Recently Gorczyca et al. \(^{71} \) studied the increase in \( m_e^*(0) \) under hydrostatic pressure.

It has been argued that the interaction energy \( E_P \) is material insensitive and is nearly a constant, between 10 and 15 eV, close to the value expected in the empty lattice model. \(^{54} \) This energy is much larger than \( E_g \) of most semiconductors. Therefore, according to Eq. (6), \( m_e^*(0) \) is approximately proportional to the direct-gap \( E_g \) for group III-V and II-VI semiconductors. In Fig. 9 we show this relationship where a universal \( E_p = 12 \) eV was used. This dependence is approximately linear for small-\( E_g \) materials. Interestingly, previously reported \( m_e^* = 0.11 m_0 \) measured from sputter-grown InN films with “optical bandgap” at 1.9 eV also falls near this dependence. \(^{7} \) This is because for those degenerately doped films, both \( m_e^* \) and \( E_g \) (the “optical bandgap”) were
measured at a Fermi level deep into the conductance band. In this case $E_s$ is raised by the Burstein–Moss effect, but $m^*_s$ is increased by the band nonparabolicity as well, and as a result they fall back at a position near the universal curve shown in Fig. 9.

2. First-principle calculations

This is not the first time in history that a much wider bandgap has been assigned erroneously to a semiconductor. For example, the fundamental bandgap of PbS had been believed to be 1.2 eV until in 1953 it was found to be only 0.4 eV.\textsuperscript{72} The narrow bandgap of InN is more puzzling as it breaks the common-cation rule. The common-cation (anion) rule states that for isovalent, common-cation (anion) semiconductors, the direct gap at the $\Gamma$ point increases as the anion (cation) atomic number decreases. The bandgap of InN at 0.64 eV is not only much smaller than the previously reported bandgap of InN but also smaller than the well-established bandgap of InP at 1.4 eV. However, the breakdown of the common-cation (anion) rule is not unusual in ionic semiconductors. As shown in Fig. 10(a), for Zn-group VI compounds the bandgap of ZnO is also smaller than that of ZnS.

According to the tight-binding model, the valence (conduction) band edge derives mainly from the bonding (antibonding) state of anion and cation $p$ ($s$) atomic orbitals.\textsuperscript{5}\textsuperscript{4} The energies of these orbitals for group III and V elements are shown in Fig. 11(a).\textsuperscript{73} The N 2$s$ orbital energy is at $-18.5$ eV, compared with P at $-14.09$ eV, and is much lower than the $s$ orbital energy of any other element in the figure. This is the main reason that leads to an exceptionally low conduction band minimum (CBM) in InN, and the breakdown of the common-cation rule. The trend of the breakdown can be seen in Fig. 10(b).\textsuperscript{74}

For the CBM of group III-N compounds, as the $s$ energy does not differ much among Al, Ga, and In, the CBM is predominantly determined by the energy of the N 2$s$ state and its weight in the CBM. Moving from AlN to GaN and to InN, the ionicity increases (Table I) and consequently the contribution of N 2$s$ state increases, resulting in the lowest CBM in InN among all group III-V semiconductors. Similarly there are only very small differences in the $p$ energy of Al, Ga, and In, and as such, the predominant factor in determining the valence band maximum (VBM) in III-N’s is the interaction between the cation $d$ orbitals and the N 2$p$ orbital. This $p$-$d$ repulsion pushes the VBM up in InN more than in GaN and AlN because the In 4$d$ level is the highest. For common-cation, In-group V compounds, it can be seen that the trend of CBM and VBM largely follows the anion $s$ and $p$ energy, respectively. Due to the small electronegativity of In, the In $s$ and $p$ orbitals contribute much less to the CBM and VBM.

The common-cation and common-anion rules cannot be accounted for by the pure chemical trend alone.\textsuperscript{74} The atomic size or volume effect also plays an important role in determining the bandgap. Semiconductors crystallize at their respective equilibrium lattice constants, which are typically quite different from each other. Therefore, the size or volume deformation contribution to the bandgap has to be considered. The volume deformation potential $\alpha_v$, i.e., the change in the bandgap with respect to a relative change in the volume, is typically negative; the direct bandgap thus increases when the lattice constant is reduced. Generally the order of the bandgaps calculated at fixed lattice constant is opposite to what is observed at the equilibrium lattice constants. The volume deformation contribution reverses this order and gives rise to the common-cation and common-anion rules. InN has a relative weak $\alpha_v$ ($-4.2$ eV) compared to other In–V compounds (e.g., $-5.9$ eV for InP) and III-N compounds (Table II). Therefore, the atomic size effect in InN is not strong enough to open the bandgap of InN, resulting in a smaller bandgap than InP and breakdown of the common-cation rule.\textsuperscript{74}

First-principle calculations of the band structure have become a powerful tool to explain and predict material prop-
erties and design new materials. They also provide results to parametrize simplified methods, such as the analytical $k \cdot p$ method discussed previously. The latter are conveniently applicable to device modeling in the envelope function scheme at low computational expense. First-principle calculations of InN have been made long before the discovery of its narrow bandgap using the standard density functional theory in the local density approximation (LDA). However, it is well known that although LDA well predicts structural parameters such as the equilibrium lattice constant, it typically severely underestimates the bandgap of semiconductors, due mostly to an incomplete cancellation of artificial self-interaction. For example, the LDA-calculated bandgap of GaAs is only −0.3 eV, much smaller than the experimental value of 1.52 eV at zero temperature. For InN in the wurtzite structure, LDA predicts a metallic state with a bandgap of ~−0.3 eV. Various methods have been attempted to correct the LDA bandgap error. Using the screened exchange approach, Schilfgaarde et al. find that the bandgaps are 1.3 and 1.4 eV for zincblende and wurtzite InN, respectively. Model GW calculation by Johnson and Ashcroft yields a bandgap of 1.79 eV for InN. Using the self-interaction correction, Vogel et al. find a corrected bandgap of 1.6 eV for the wurtzite InN. Quasiparticle calculation using the GW approximation gives a bandgap value of only 0.01 eV (Ref. 77) or 0.02–0.05 eV.

More efforts have been devoted to the band structure calculation of InN after the experimental discovery of its narrow bandgap. Using a LDA-based semiempirical method, Wei et al. calculated the bandgap of InN and systematically studied the chemical trends of the bandgap and other band parameters in group-III nitrides. Bandgaps of 0.70 and 0.85 eV was found for zincblende and wurtzite InN, respectively. In their approach they correct the LDA bandgap error by adding to the LDA potential a δ-function-like external potential inside the muffin-tin spheres, and perform the calculation self-consistently. The bandgap obtained by this method is much closer to the real value. Alternatively, using a special type of pseudopotentials which account for self-interaction corrections, Bechstedt and Furthmüller obtained a bandgap of 0.59 and 0.81 eV for zincblende and wurtzite InN, respectively. Bagayoko et al. obtained a bandgap of 0.65 eV (Ref. 83) and 0.88 eV (Ref. 84) for zincblende and wurtzite InN, respectively.

Very recently, Rinke et al. employed a single-iteration $GW$ method based on density functional theory to determine the basic band parameters of group-III nitrides. Their calculations were carried out at the experimental lattice constants; their method is fully self-interaction free and therefore expected to effectively correct the LDA error. A consistent set of band parameters were found for AlN, GaN, and InN. Specifically, the fundamental bandgap of InN was calculated to be 0.69 and 0.53 eV for the wurtzite and zincblende phases, respectively. As these values are the closest to experimental data, we recommend their calculated band parameters in Tables I and II. Their calculated conduction and valence bands in the vicinity of the $\Gamma$ point are shown in Fig. 12. These bands are very well reproduced by the $k \cdot p$ formulation if the recommended band parameters in Table II are used. Compared to the $k \cdot p$ calculated bands shown in Fig. 6, it can be seen that the calculated $E_g=0.69$ eV, $m_e/m_0=0.065$ (||) or 0.068 (⊥), and $E_F=8.7$ eV (||) or 8.8 eV (⊥), all agreeing very well with up-to-date experimental values $E_g=0.69$ eV, $m_e/m_0=0.07$, and $E_F=10$ eV. In addition, the first-principle calculations provide many band parameters that are not yet experimentally available, such as the crystal-field splitting and spin-orbit splitting, deformation potentials, and the hole effective masses. These parameters are listed in Table II.

Most of these theoretical works only present the band structure near the $\Gamma$ point or along the $\Gamma$-$M$ and $\Gamma$-$A$ lines. Figure 13 shows the band structure of InN in the entire Brillouin zone calculated by Fritsch et al. within the empirical pseudopotential method by exploiting the transferability of ionic model potential parameters. Their calculation gives bandgap values of 0.79 and 0.59 eV for wurtzite and zincblende InN, respectively. From these dispersion curves, critical points at higher energies can be also identified. These critical points correspond to direct optical transitions with high transition probabilities. These transitions typically occur at Van Hove singularities in the joint conduction-valence band density of states where $E_C(k)-E_V(k)$ takes a local minimum.

**FIG. 12.** (Color online) First-principle calculation of the conduction and valence bands of wurtzite InN near the $\Gamma$ point. Analytical dispersions using $k \cdot p$ parameters listed in Table II agree well with these curves. Reference 55.

**FIG. 13.** (Color online) First-principle calculation of the band structure of wurtzite InN in the entire Brillouin zone. The Fermi stabilization level ($E_{FS}$) is also shown (see Sec. III B). Reference 85.
calculations in Fig. 13 if the assignments listed in Table I are used. Unlike the blueshift of the bandgap due to the 011101-10 Junqiao Wu J. Appl. Phys. shape,44 and labeled as transition 7.87, and 8.70 eV, respectively. They are determined by fitting the critical points in InGaN and InAlN alloys. 0.56 at room temperature.89 These values are recommended to be independent of the doping level.88 This is expected from the fact that these energies involve optical transitions deep in the valence band. The direct bandgap of a wurtzite semiconductor is only in its third-nearest-neighbor atomic arrangement; consequently these two structures are quite close in total energy.75 The direct bandgap of a wurtzite semiconductor is typically ~0.1 eV wider than its zincblende polymorph. Schoermann et al. grew zincblende InN using MBE and measured the bandgap to be 0.61 at low temperature and 0.56 at room temperature.89 These values are recommended and listed together with other physical properties of zincblende group-III nitrides in Table IV.

C. Carrier recombination dynamics

The understanding of the physics and dynamics of carrier recombination is crucial for the development of InN-based devices. The recombination physics can be studied by various time-resolved pump-probe techniques. Figure 15(a) shows the differential transmission transients of three InN films with distinctly different doping levels reported by Chen et al.90 The probe energy was tuned to the absorption edge (E₂). The pump pulse is shorter than 1 ps and its intensity was controlled such that the injected carrier density is much lower than the original equilibrium carrier concentration in the sample. It is clear that these transients can be described by a single exponential decay, with a nonequilibrium carrier lifetime (τ) depending on doping level and temperature. Similar dynamics was also probed using transient photoreflectance technique.91 The room-temperature carrier lifetime determined in these studies is plotted together as a function of the electron concentration in Fig. 15(b). It can be seen, not surprisingly, that the carrier lifetime is approximately inversely proportional to the free electron concentration. This effect is analogous to the rapid decrease in electron mobility with increasing electron concentration in InN;92 both effects are dependent on impurities and defects, which scatter free carriers (in the case of electrical transport) or mediate carrier recombination (in the case of optical transitions).

The photogenerated electrons and holes recombine mainly through three channels: nonradiative defect-mediated, radiative interband, and nonradiative Auger recombination. The total recombination rate is written as

\[ D_{\text{joint}}(E_c - E_v) \sim \int \frac{dS_k}{|V_k|} \left( E_c(k) - E_v(k) \right) \tag{11} \]

Experimentally these critical point energies can be determined from the complex dielectric functions measured in the 0–10 eV range using ellipsometry.44,45,86 Such a set of experimental dielectric function curves are shown in Fig. 14.44 In addition to the direct bandgap (E₁ or E₂) at ~0.7 eV, five critical points are clearly seen at energies 4.88, 5.35, 6.05, 7.87, and 8.70 eV, respectively. They are determined by fitting the dielectric function curves with a third-derivative line shape,44 and labeled as transition A, E₁, E₂, E₃, and E₄, respectively (after Ref. 87). These energies agree well with calculations in Fig. 13 if the assignments listed in Table I are used.88 Unlike the blueshift of the bandgap due to the Burstein–Moss effect, these energies were found to be independent of the doping level.88 This is expected from the fact that these energies involve optical transitions deep in the conduction and valence bands far from the Fermi level. In Sec. III A we will discuss the composition dependence of these critical points in InGaN and InAlN alloys.

The zincblende structure differs from the wurtzite one only in its third-nearest-neighbor atomic arrangement; consequently these two structures are quite close in total energy.75 The direct bandgap of a wurtzite semiconductor is typically ~0.1 eV wider than its zincblende polymorph. Schoermann et al. grew zincblende InN using MBE and measured the bandgap to be 0.61 at low temperature and 0.56 at room temperature.89 These values are recommended and listed together with other physical properties of zincblende group-III nitrides in Table IV.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>AlN–GaN</th>
<th>GaN–InN</th>
<th>InN–AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Valence band offset, ΔEᵥ (eV)</td>
<td>−0.7a</td>
<td>−1.1b</td>
<td>1.8c</td>
</tr>
<tr>
<td>Alloy bandgap bowing (eV)</td>
<td>0.6b</td>
<td>1.4c</td>
<td>5.0d</td>
</tr>
<tr>
<td>Alloy critical point A bowing (eV)</td>
<td>0.8b</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alloy critical point E₁ bowing (eV)</td>
<td>0.2c</td>
<td>1.1d</td>
<td>1.8e</td>
</tr>
<tr>
<td>Alloy critical point E₂ bowing (eV)</td>
<td>0.1c</td>
<td>1.0d</td>
<td>2.7e</td>
</tr>
<tr>
<td>Alloy critical point E₃ bowing (eV)</td>
<td>0.5c</td>
<td>0.7d</td>
<td></td>
</tr>
</tbody>
</table>

References: 90, 91, 92.
function of temperature. The solid line indicates a power law fit to sample A. The two red dots show the measured total lifetime ($\tau$) in sample A. Reference 90.

\[
\frac{1}{\tau} = \frac{1}{\tau_{\text{defect}}} + \frac{1}{\tau_{\text{radiative}}} + \frac{1}{\tau_{\text{Auger}}} = \sigma \bar{v} N_{\text{defect}} + B_{\text{radiative}} N_{\text{Auger}} + B_{\text{Auger}} N_{\text{radiative}}^2,
\]

where $\sigma$ and $\bar{v}$ are the capture cross section and mean velocity of free carriers, respectively. The fact that the overall slope of $\tau$ versus $n$ is closer to $-1$ than to $-2$ in Fig. 15(b) suggests that the Auger effect is not a dominant recombination mechanism in InN, at least not for the pumping intensities used in these experiments.

Using Eq. (12), Chen et al. estimated the radiative recombination coefficient to be $B_{\text{radiative}} = (2.6 \pm 0.5) \times 10^{-11}$ cm$^3$ s$^{-1}$ at 300 K for InN. By relating the temperature dependence of PL intensity to the radiative recombination rate, they further extracted the temperature-dependent radiative recombination lifetime, $\tau_{\text{radiative}}$, as shown in Fig. 16, where the total lifetime ($\tau$) at 20 and 300 K for sample A are also shown for comparison. It is clear from Fig. 16 that the defect-mediated nonradiative recombination is largely inactive at low temperatures, while it becomes dominant at higher temperatures. The derived $\tau_{\text{radiative}}$ is strongly temperature dependent and scales with $\sim T^{\gamma}$, where $\gamma$ is close to 3/2. This is consistent with the Lasher–Stern model which predicts that for bimolecular radiative recombination in direct bandgap semiconductors, $B_{\text{radiative}} \sim T^{-3/2}$ when the momentum selection rule holds.

Analyzing the differential transmission transient in Fig. 15(a) in energy (rather than time) domain reveals that although the signal at peak and lower energies exhibits a single-exponent decay which is recombination related, for the high-energy shoulder, a fast decay ($\sim 10$ ps) occurs prior to this carrier recombination [Fig. 17(a)]. This fast decay is attributed to hot-carrier thermalization. Assuming a Maxwell–Boltzmann distribution of hot electrons and holes, the carrier temperature can be derived from the slope of the high-energy shoulder in Fig. 17(a). The carrier temperature obtained by this means is plotted as a function of time in Fig. 17(b), showing a cooling of photoexcited carriers within $\sim 10$ ps when the pumping source is turned off. This cooling is explained by a thermalization process involving carrier-LO phonon scattering, as shown by the fitting curve in Fig. 17(b). More discussions on this process will be presented in Sec. III C.

III. InGaN AND InAlN ALLOYS

A. Bandgap and band alignment

1. Bowing of bandgap and critical point energies

The re-evaluation of the bandgap of InN brings new insights on studies of group III-nitride alloys that were already intensively investigated for their application in optoelectronics. Figure 18 shows the room-temperature absorption curves for In-rich InGaN (Ref. 92) and InAlN (Ref. 94) alloys over a wide range of compositions. As expected, the absorption edge shows a rapid blueshift from the bandgap of InN with increasing Ga or Al content.

The bandgaps of In$_{1-x}$Ga$_x$N and In$_{1-x}$Al$_x$N are plotted as a function of $x$ in Fig. 19(a). Representative data on the Ga or Al-rich side from literature are also shown for completion of the entire composition range. As shown by the solid
lines in Fig. 19(a), the bandgap of In$_{1-x}$Ga$_x$N and In$_{1-y}$Al$_y$N over the entire composition range can be well fit by the following standard bowing equation:

$$E_g(x) = E_g(0) \cdot (1 - x) + E_g(1) \cdot x - b \cdot x \cdot (1 - x).$$  \hspace{1cm} (13)

The bowing parameter is found to be $b = 1.4 \pm 0.1$ eV (Ref. 95) for In$_{1-x}$Ga$_x$N and $5.0 \pm 0.5$ for In$_{1-y}$Al$_y$N. A bowing parameter as large as 2.63 eV is assumed. Even when a narrow bandgap of InN was used, different experimental values of $b$ equal to 2.5 eV, 2.3 eV, and 1.8 eV (Ref. 101) have been reported. As pointed out by Caetano et al., it is critical to measure $E_g$ over a large range of composition in order to have an accurate assessment of $b$. Other effects such as strain, doping and composition fluctuation can also affect the measured bandgap bowing. On the other hand, the large $b$ for In$_{1-y}$Al$_y$N is related to its much wider bandgap range, and the large uncertainty of $b$ comes from the more scattered data measured in this wide range of $E_g$. For discussion on the indirect bandgaps of group-III nitrides and their bowing, the readers are referred to Ref. 40.

It is inspiring to plot the bandgap bowing as a function of lattice constant instead of composition, so that the three alloys In$_{1-x}$Ga$_x$N, In$_{1-y}$Al$_y$N, and Al$_{1-y}$Ga$_y$N can be plotted on the same coordinates. To do so, we assume a linear dependence of the lattice constant on composition following Vegard's law. The bandgap bowing in Fig. 19(a) is consequently mapped to a bowing as a function of in-plane lattice constant, as shown in Fig. 19(b). For the available range of experimental data, the bandgap of In$_{1-x}$Al$_x$N falls practically onto the same curve of In$_{1-x}$Ga$_x$N. Therefore, In-rich In$_{1-x}$Ga$_x$N and In$_{1-y}$Al$_y$N will have the same bandgap if their compositions are tuned separately to match their lattice constant. The condition for such a concurrent lattice and bandgap match is $x \approx 1.25y$. It has been recently shown that the InGaN and InAlN alloys have good thermoelectric properties. Even though In$_{1-x}$Ga$_x$N and In$_{1-y}$Al$_y$N have equal bandgaps at lattice-matched conditions, their acoustic properties such as thermal conductivity can be quite different. If their CBM and VBM are shown to align well at this lattice-matched condition, superlattices of In$_{1-x}$Ga$_x$N/In$_{1-y}$Al$_y$N would be an ideal electronically and lattice matched but acoustically mismatched system. Such systems can be of great interest in high-performance thermoelectrics.

Similar to the bandgap, the high-energy critical points have also been measured as a function of composition for InAlN (Ref. 43) and InGaN (Ref. 45) using spectroscopic ellipsometry. The results are shown in Fig. 20. The bowing parameter for the energy of each of these critical points is determined by fitting with the bowing equation and listed in Table III. With this information, the complex dielectric function of the InGaN and InAlN alloys in the entire composition range can be parametrized with the standard analytical model.

### Table IV. Recommended values of basic physical parameters of zincblende InN, AlN, and GaN.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>AlN</th>
<th>GaN</th>
<th>InN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constant $a$ (nm)</td>
<td>0.438$^a$</td>
<td>0.450$^a$</td>
<td>0.498$^a$</td>
</tr>
<tr>
<td>Bandgap $E_g(T=0)$ (eV)</td>
<td>5.4$^a$</td>
<td>3.3$^a$</td>
<td>0.6$^b$</td>
</tr>
<tr>
<td>Vashni parameter $\alpha$ (meV/K)</td>
<td>0.593$^a$</td>
<td>0.62$^a$</td>
<td></td>
</tr>
<tr>
<td>Vashni parameter $\beta$ (K)</td>
<td>600$^a$</td>
<td>0.593$^a$</td>
<td>0.62$^a$</td>
</tr>
<tr>
<td>Electron effective mass $m^*/m_0$</td>
<td>0.32$^c$</td>
<td>0.19$^c$</td>
<td>0.05$^c$</td>
</tr>
<tr>
<td>$\gamma_1$</td>
<td>1.45$^c$</td>
<td>2.51$^c$</td>
<td>6.82$^c$</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>0.35$^c$</td>
<td>0.64$^c$</td>
<td>2.81$^c$</td>
</tr>
<tr>
<td>$\gamma_3$</td>
<td>0.60$^c$</td>
<td>0.98$^c$</td>
<td>3.12$^c$</td>
</tr>
<tr>
<td>$m_{hh}^{[100]}(|m_0)$</td>
<td>1.33$^c$</td>
<td>0.81$^c$</td>
<td>0.84$^c$</td>
</tr>
<tr>
<td>$m_{hh}^{[110]}(|m_0)$</td>
<td>2.63$^c$</td>
<td>1.38$^c$</td>
<td>1.37$^c$</td>
</tr>
<tr>
<td>$m_{hh}^{[111]}(|m_0)$</td>
<td>3.91$^c$</td>
<td>1.81$^c$</td>
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<td>$m_{hh}^{[001]}(|m_0)$</td>
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<td>0.27$^c$</td>
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<td>$m_{lh}^{[100]}(|m_0)$</td>
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<td>0.23$^c$</td>
<td>0.08$^c$</td>
</tr>
<tr>
<td>$m_{lh}^{[110]}(|m_0)$</td>
<td>0.38$^c$</td>
<td>0.22$^c$</td>
<td>0.08$^c$</td>
</tr>
<tr>
<td>$m_{lh}^{[111]}(|m_0)$</td>
<td>0.47$^c$</td>
<td>0.29$^c$</td>
<td>0.3$^c$</td>
</tr>
<tr>
<td>$\Delta_n$ (meV)</td>
<td>19$^c$</td>
<td>17$^c$</td>
<td>5$^c$</td>
</tr>
<tr>
<td>Volume deformation potential $a_V$ (eV)</td>
<td>$-10^c$</td>
<td>$-7.3^c$</td>
<td>$-3.8^c$</td>
</tr>
<tr>
<td>$E_F$ (eV)</td>
<td>23.8$^a$</td>
<td>16.9$^a$</td>
<td>11.4$^a$</td>
</tr>
<tr>
<td>TO phonon (1/cm)</td>
<td>655$^d$</td>
<td>555$^d$</td>
<td>472$^d$</td>
</tr>
<tr>
<td>LO phonon (1/cm)</td>
<td>902$^d$</td>
<td>742$^d$</td>
<td>586$^d$</td>
</tr>
</tbody>
</table>

1$^a$Reference 40.  
2$^b$Reference 89.  
3$^c$Reference 55.  
4$^d$Reference 47.
2. Band alignment and offset

The band offset between group-III nitrides has been a focus of theoretical and experimental investigations long before the revision of the bandgap of InN. Because what is responsible for the revision is the conduction band-filling effect, previous studies of the valence band offset between InN and other nitrides are considered still valid. However, there is no consensus on the valence band offset between these materials owing to complications such as piezoelectric strain, and spontaneous polarization effects.40 Due to these effects the offset may be growth sequence dependent, i.e., different between the heterojunctions of A on B and B on A.108 A wide range of values have been reported for the natural valence band offset between wurtzite InN and GaN. For example, on the calculation side, 0.3 eV,109 0.48 eV,110 0.7 eV,111 and 1.27 eV,112 and experimentally 0.5 eV,113 0.58 eV,114 0.78 eV,115 1.04 eV (In/Ga polar), or 0.54 eV (N polar),108 1.05 eV,105 and 1.1 eV (Ref. 116) have been reported. We recommend the results of Martin et al. measured using x-ray photoemission spectroscopy,105 because they systematically measured all three types of heterojunctions and reached self-consistent values. In their experiments the VBM of wurtzite InN was found to be −1.1 eV above that of GaN (Ref. 105) after corrections to strain and piezoelectric effects. Therefore a type-I band alignment with ΔEv/ΔEg=0.38 exists in this system. This result and the GaN/AIN and InN/AIN band offsets are listed in Table III. The transitivity rule is clearly satisfied in these offset values. However, the readers are advised to take caution in using these values. Further development in the measurements of group III-nitride band offset is expected.

B. Electronic properties

1. Native defects and n-type doping

GaN is notoriously difficult to be doped p type. The doping disparity is even more pronounced for InN. As-grown InN has a strong propensity to be unintentionally n type, a behavior similar to GaN before better control of its growth and doping was achieved. The origin of the n-type conductivity in InN is still a topic of debate and investigation. First-principle calculations show that the nitrogen vacancy (VN) is the lowest energy native defects, and can be a major source of free electrons in n type or compensating donors in p-type InN.117–119 This view is supported by some experimental evidence.26,120,121 Indium vacancy has also been found to play a role in the conductivity in InN.122 Additionally, hydrogen in InN was predicted to act exclusively as a shallow single (when interstitial) or double (when substitutional) donor,123 owing to the fact that H0 and H+ are always higher in energy than H+.124 Experimental studies seem to support this prediction.125–128 This is in contrast to the amphoteric behavior of hydrogen in GaN and AlN, where it is stable as a donor in p type and as an acceptor in n-type material, always compensating the prevailing conductivity.129 Oxygen and silicon are expected to have a lower energy than VN in n-type InN, therefore potentially a significant source of free electrons.117,130 However, it was demonstrated by experiments combining Hall effect and secondary ion mass spectroscopy that O and H alone cannot fully account for the free electron concentration in unintentionally n-type InN.65 Therefore native defects may play a critical role in the n-type unintentional doping. Besides point defects, edge-type threading dislocations131 and VND segregated along dislocation lines132 have been suggested to be a dominant source of free electrons in InN. Given the uncertainties with the source of background electrons in InN, more studies are needed before the n-type doping in In-rich InGaN can be fully understood.

2. p-type doping

p-type doping of InN and In-rich InGaN has been the focus of intense research efforts. Realization of their opto-electronic applications depends critically on the success of p-type doping. Mg is the most studied dopant acting as a possible acceptor in InN. Since evidence for p-type doping in InN was reported for the first time by Jones et al. in 2006,133 many groups have confirmed and characterized hole conduction in Mg-doped InN.134–140 Unlike undoped or n-type InN films, these films typically exhibit no or extremely weak photoluminescence at room temperature. Using low-temperature photoluminescence spectroscopy, Wang et al.136 determined the acceptor ionization energy of Mg in InN to be about 61 meV, much shallower than 110 meV estimated by Anderson et al.,134 but comparable to the acceptor binding energy of 50–55 meV reported by Klochikhim et al.141 and 60 meV reported by Khan et al.42 However, due to the background electron doping or surface electron accumulation (discussed below), all these Mg-doped InN films exhibit net n-type conductivity in direct Hall effect measurements. There seems to be a window of Mg concentration from 1018 to 3×1019 cm−3 that produces bulk p-type activity.138 Outside this window, incorporation of Mg only partially compensates the background electron doping. Miller et al.142 observed the sign difference of thermopower between undoped and Mg-doped InN. Wang et al.137 estimated the hole mobility to be 17–36 cm2 V−1 s−1 using the hot probe method.145 The binding energy of Mg acceptor, determined that most of the Mg atoms occupy substitutional In sites. p-type activity in the bulk of In-rich InxGa1−xN alloys was also reported by Chang et al.144 for In content up to 0.56 using Hall effect, King et al.135 for 0<x<1 using x-ray photoelectron spectroscopy, and Schaff et al. for 0<x<1 using the hot probe method.145 The binding energy of Mg acceptor was shown to decrease from GaN to InN.144 A chemical trend is seen in the Mg acceptor binding energy from AlN to GaN (Ref. 41) and to InN, as listed in Table I.

3. Surface properties

Despite the clear evidence of free holes in the bulk, p-type conductivity has not been directly observed in Mg-doped InN by Hall effect. The reason is that the surface of InN is strongly electron accumulated regardless of the bulk doping, a direct consequence of the surface Fermi level being pinned deep in the conduction band.

The surface Fermi level pinning effect can be described by the amphoteric defect model developed by Walukiewicz.146 In this model the states that pin the Fermi
level \( (E_F) \) tend to fall near a universal energy level, known as the Fermi stabilization energy \( (E_{FS}) \). In compound semiconductors the formation energy of acceptor-type (donor-type) native defects, such as cation (anion) vacancies, decreases linearly as the Fermi level moves toward the conduction (valence) band. \( E_{FS} \) is defined as the crossover point of \( E_F \) when these two energies are equal. In the bulk, \( E_{FS} \) is the energy position where \( E_F \) tends to stabilize at by the creation of native defects that compensates the external doping. For the surface defect states associated with dangling bonds, surface reconstruction, contaminations, etc., the surface Fermi level tends toward \( E_{FS} \) to neutralize these states. \( E_{FS} \) lies \( \sim -4.9 \) eV below the vacuum level, and falls into the bandgap for most semiconductors. However, in InN and In-rich InGaN and InAlN, due to their exceptionally low CBM, \( E_{FS} \) is located deep in the conduction band, about 0.8 eV above the CBM, or \( \sim -1.5 \) eV above the VBM of InN as shown in Fig. 21 and Fig. 11(b). This energy configuration causes strong electron accumulation near the surface, hiding the \( p \)-type activity in the acceptor-doped bulk. Electrical properties, measured by Hall effect, are determined by electron transport in this surface layer rather than in the bulk of the sample. \( E_{FS} \) crosses the CBM of In\(_{1-x}\)Ga\(_x\)N at approximately \( x \approx 0.6 \). Therefore, a surface electron accumulation is expected for \( p \) fraction exceeding \( \sim 0.4 \), while a surface depletion is expected for the rest of the composition. This effect has been experimentally confirmed by King et al. using x-ray photoemission spectroscopy.\(^{147,148}\) They found that the transition from surface accumulation to depletion occurs at In fraction \( \sim 0.43 \) for \( n \)-type InGaN, and from surface inversion to hole depletion at In fraction \( \sim 0.59 \) for \( p \)-InGaN. A deviation of surface Fermi level pinning from \( E_{FS} \) was measured across the composition range. Similar surface electron accumulation was observed in InAlN alloys.\(^{149}\) As shown in Fig. 11(b), a similar effect is expected in InAs as well, and indeed, a strong surface electron accumulation has been observed in InAs.\(^{150}\)

The surface accumulation in InN was first suggested by Lu et al.\(^{151}\) and Rickert et al.\(^{152}\) and directly probed by Mahboob et al. using high-resolution electron-energy-loss spectroscopy.\(^{153,154}\) In the studies of Mahboob et al. the physics is described in terms of the branch-point energy \( (E_B) \) instead.\(^{155,156}\) \( E_B \) is an energy level used to describe the pinning position of the Fermi level by defect states. These states are typically deep states that are spatially localized and therefore sample a substantial portion of the Brillouin zone, not just the band edges as hydrogenlike states do. The position of \( E_B \) in the band structure is determined by calculating the average midgap energy across the entire Brillouin zone,\(^{155}\) as shown schematically in Fig. 13. \( E_B \) tends to coincide with \( E_{FS} \) because both are defined by deep defect states, regardless of their detailed nature and origin.

Given the surface Fermi level position, the band bending and charge distribution near the surface can be calculated by solving the Poisson equation numerically. Complications arise from the conduction band nonparabolicity,\(^{20}\) band renormalization,\(^{20}\) and quantum effects\(^{154,157,158}\) at such high electron concentrations over a small depth. An example of the calculation is shown in Fig. 22, where the quantum confinement effect is neglected.\(^{139}\) It can be seen that regardless of the bulk doping type and concentration, a surface electron accumulation (or inversion in the case of \( p \)-InN) exists with concentrations above \( 10^{20} \) cm\(^{-3} \) within a depth \( \sim 5 \) nm. Especially, for \( p \)-InN a \( n-p \) junction forms on the surface that prevents electrical contact with the bulk. The surface sheet electron concentration is as high as \( \sim 10^{13} \) cm\(^{-2} \), the strongest native surface electron accumulation among any III-V semiconductor. Quantum confinement and quantized energy levels were observed in the surface layer by Colakeroz et al. using angle-resolved photoemission spectroscopy, as shown in Fig. 23,\(^{157}\) and quantitatively calculated by King et al.\(^{159}\)

The degree of band bending and sheet electron density can be also modulated by electrolyte gating as discussed below. Such a tunable two-dimensional electron gas naturally forming on the InN surface offers a simple system to probe interesting physics and explore new applications.

We note that the surface Fermi level pinning above the CBM in InN was explained by density functional theory calculations performed by Van de Walle et al.\(^{160}\) The authors also predict an absence of such an electron accumulation on the nonpolar InN (1100) and (11\( \bar{2} \)) surfaces, and on polar surfaces if processed to consist purely of In–N dimers. InN films with different polarities were first grown and studied by
Xu et al., King et al. reported the universality of electron accumulation on both polar and nonpolar InN surfaces, although Gwo et al. showed evidence of absence of accumulation layer on in situ cleaved nonpolar InN surfaces.

Owing to the surface electron accumulation layer, direct Hall effect only measures the free carrier concentration averaged over the depth weighted by mobility. For nonuniform charge distributions such as these, capacitance-voltage (CV) profiling yields more information as it probes the net charge concentration as a function of depth. However, for InN the surface $E_F$ is pinned above CBM, as such the required Schottky contacts for conventional CV profiling cannot be achieved with metals. Instead, a liquid electrolyte has been used to form a rectifying contact in a metal-insulator-semiconductor configuration, a technique known as electrochemical CV (ECV) profiling. A bias voltage ($V_{bias}$) applied to the electrolyte with respect to the grounded sample bulk shifts the surface Fermi level to $E_F = E_{FS} + V_{bias}$. Thus a negative $V_{bias}$ causes the surface energy bands to move upward relative to $E_{FS}$, making the surface bands bend less than in Figs. 22(a) and 22(b). At sufficiently large negative $V_{bias}$, a flat band, followed by surface depletion, and eventually inversion band configuration can be realized for both $n$- and $p$-doped films, provided that the electrolyte and film junction do not break down at these voltages. The capacitance ($C$) of the surface layer is monitored and plotted as a function of $V_{bias}$. Unlike the normal Mott–Schottky plot where $1/C^2$ is plotted against $V_{bias}$ and the slope measures the doping level, in this situation a nonmonotonic behavior is seen on the $1/C^2$ versus $V_{bias}$ plot. The peak corresponds to the $V_{bias}$ when the surface $E_F$ is displaced into the bandgap, such that the total space charge $Q$ becomes desensitized to the variation of $V_{bias}$, because $E_F$ is too far from both CBM and VBM to populate or depopulate the conduction or valence bands. For this $V_{bias}$, the system has the smallest $C = dQ/dV_{bias}$ and thus has a peak in $1/C^2$. The Mott–Schottky plot for a $n$- and a $p$-type InN film is depicted in Fig. 24, and compared to the theoretical curves and band configuration calculated by Yim et al.

The peak height ($1/C^2$ at peak) is related to the bulk doping level ($N_d$ or $N_a$), while the peak position ($V_{bias}$ of peak) can be used to identify the bulk doping type. The latter is because the position of $E_F$ at the peak relative to the surface CBM and VBM is not the same for $n$- and $p$-doped films. It is closer to VBM (CBM) on the surface for $n$ ($p$)-doped InN, resulting in a peak at more negative $V_{bias}$ for $n$-doped films than for $p$-doped ones. Namely, the surface $E_F$ position where $Q$ is the least sensitive to changes in $V_{bias}$ is not exactly at the midgap; instead, it is pushed away from the doped band since $Q$ would change rapidly at the onset of depletion of that band. This effect breaks the symmetry of the surface $E_F$ in the bandgap, and quantitatively identifies the type of bulk doping by the position of the $1/C^2$ peak. As ECV is essentially the only technique for directly measuring the doping level in the presence of surface accumulation in narrow-gap semiconductors such as InN and InAs, this model provides a general guideline and calibration for analyzing doping in narrow-gap semiconductors. In Ref. 139 this model is also extended to InGaN alloys. Recent ECV experiments by Wang et al. suggest that charges at surface states within the bandgap of InN also affect the capacitance, and a correction is needed to account for these states in ECV experiments. Brown et al. quantitatively probed the change in surface layer conduction using electrolyte-gated Hall effect.

4. Radiation resistance

In view of the important role of native defects in the doping behavior of InN and InGaN, energetic-particle irradiation was used to systematically introduce point defects at controlled concentrations. Radiation damage by different types of energetic particles can be calibrated using a single parameter known as the displacement damage dose ($D_d$). Electrons, protons, and $^4$He$^+$ were used to produce a $D_d$ spanning 5 decades. Most materials such as GaAs, GaInP, and GaN rapidly become electrically insulating with increasing $D_d$. In stark contrast, the electrical conduction of...
InN and In-rich InGaN does not deteriorate even at extraordinarily high doses of radiation. In fact, the free electron concentration increases with increasing radiation dose and saturates at sufficiently high doses, as shown in Fig. 25.\(^{166}\) The saturation is consistent with the amphoteric defect model which predicts a final stabilization position of \(E_F\) at \(E_{FS}\), above the CBM of InN and In-rich InGaN.\(^{166}\) Positron annihilation spectroscopy measurements suggest that negatively charged N interstitials are generated at high rate by the irradiation, and may be the defects that ultimately limit the free electron concentration at high irradiation dose.\(^{167}\) The electron mobility and minority carrier lifetime were also found to be much less sensitive to the irradiation than for GaAs and GaInP, which are the materials currently used in high-efficiency multi-junction solar cells.\(^{167}\) This superior radiation resistance of In-rich InGaN is desirable for device applications in radiative environments such as outer space and nuclear reactors.

5. Transport properties

The surface electron accumulation layer is expected to have different transport properties from the bulk, due to its high electron concentration, confined electron wave function in the out-of-plane direction, and its proximity to surface scattering centers. Using quantitative mobility spectrum analysis in variable magnetic field Hall measurements, the surface layer conduction has been deconvoluted from the bulk conduction assuming a two-layer conduction model. The surface layer and bulk mobility at room temperature for an InN film were found to be \(\sim 500\) and \(\sim 3500\) cm\(^2\)/V s, respectively.\(^{168}\) Using this method for a Mg-doped InN film, a heavy-hole and light-hole conduction at distinctly different mobilities was separated from electron conduction which is attributed to the surface electron inversion layer.\(^{134}\) Electric field dependence of the mobility of InN has been studied theoretically by Monte Carlo modeling, and a maximum mobility of 10 000 cm\(^2\)/V s (Ref. 169) and 14 000 cm\(^2\)/V s (Ref. 170) has been predicted for low carrier concentrations. Field-induced nonequilibrium electron distribution and transport in InN has been measured by Liang et al. and Tsen et al. using picosecond Raman spectroscopy, where a drift velocity as high as \((5 \times 10^7)\) to \((2 \times 10^9)\) cm/s has been observed.\(^{171,172}\) For a review on the comparison of high-field transport properties of group-III nitrides, see Ref. 173. We also note that Inushima et al. reported superconductivity\(^{174}\) for a large magnetoresistance in InN (Ref. 175) at low temperatures (<2 K).

For not intentionally doped InN, Hall effect always shows electron conduction, and the electron concentration and mobility are a strong function of film thickness. Figure 26(a) shows a summary given by Schaff et al.\(^{145}\) It was pointed out that the electron concentration follows defect density caused by lattice mismatch, which decreases for thicker films. Therefore, native defects, not impurities, and contaminations, are the prominent electron sources in these films.\(^{145,176}\) A strong correlation between the electron mobility and concentration was observed in as-grown InN, as shown in Fig. 26(b). The energetic-particle irradiated samples also approximately follow the same dependence, motivating the use of irradiation for a controlled study of the behavior of native defects in InN and its alloys.\(^{176,177}\)

Using a variational procedure, Hsu et al. calculated various electron scattering mechanisms in InN and its alloys.\(^{178}\) By fitting their calculated results to experimental mobility data, they conclude that in pure InN, Coulomb scattering from charged centers is the dominant mobility-limiting mechanism, although scattering from polar optical phonons and piezoelectric mode acoustic phonons becomes important at low doping concentrations (<10 \(^{18}\) cm\(^{-3}\)) and at high temperatures (>400 K). In InGaN and InAlN, Coulomb and alloy disorder scattering are the dominant processes, as shown in Fig. 27. The defects resulting from irradiation of InN and its alloys are found to be triply charged donors. Using Monte Carlo simulations, Yu et al. modeled the effects of dislocations on electron transport in InN.\(^{179}\) They con-
close to the theoretical value predicted by Bellaiche et al.\textsuperscript{183} For InGaN alloys the pressure coefficient is in between the two theoretical predictions by Wei and Zunger\textsuperscript{58} and Christensen and Gorczyca.\textsuperscript{192} Considering the pressure coefficient of GaN to be $\sim 4$ meV/kbar,\textsuperscript{180} it is interesting to see how $dE_g/dP$ of InGaN increases from InN to GaN. Recently Franssen et al. presented experimental and theoretical results showing that $dE_g/dP$ has a nonlinear dependence on the Ga fraction, as shown in Fig. 28.\textsuperscript{61}

$$dE_g/dP$$ of In$_{0.75}$Al$_{0.25}$N was measured to be $\sim 3.5$ meV/kbar, and extrapolates to a value of $\sim 5$ meV/kbar at $x=1$; this agrees well with the pressure coefficient of AlN determined from absorption experiments.\textsuperscript{60} Note that the pressure coefficients of the group-III nitrides are much smaller than those of other III-V compounds. For example, $dE_g/dP=11$ meV/kbar for GaAs (Ref. 184) is almost three times larger than that for GaN. This trend can be attributed to the larger ionicity of the group-III nitrides due to the high electronegativity of N. In group III-V semiconductors, higher ionicity typically leads to smaller pressure coefficients.\textsuperscript{185} The Phillips ionicity is 0.31 for GaAs and is significantly smaller than 0.50 for GaN. The trend applies to group-III nitrides as well, among which larger cations give higher ionicity [AlN $f_i=0.449$, GaN $f_i=0.500$, and InN $f_i=0.578$ (Ref. 36)] and thus smaller pressure coefficients.

The volume deformation potential of the bandgap ($a_V = dE_g/d(\ln V)$) in group-III nitrides has been calculated by various groups. These calculations generally give good agreements, such as $a_V=-4.1$, $-7.8$, $-8.8$ eV,\textsuperscript{58} $-3.7$, $-7.4$, and $-10.2$ eV,\textsuperscript{58} $-3.1$, $-7.7$, and $-9.8$ eV,\textsuperscript{186} and $-4.2$, $-7.6$, and $-9.8$ eV (Ref. 55) for InN, GaN, and AlN, respectively. The decrease in $|a_V|$ with increasing ionicity is evident.\textsuperscript{58} The bulk modulus ($B=-dP/d(\ln V)$) has been theoretically calculated as well. Experimental results of $B$ scatter within a wide range between 1260–1480 kbar for InN,\textsuperscript{32} 1880–2450 kbar for GaN,\textsuperscript{187,188} and 1850–2079 kbar for AlN.\textsuperscript{189–191} In Table III we recommend Wei and Zunger’s results as they calculated both $a_V$ and $B$ systematically.\textsuperscript{58}

### 2. Piezoelectric properties

The lack of center of symmetry in group-III nitrides results in piezoelectricity. They also exhibit spontaneous polarization with polarity determined by the terminating anion or cation plane on the surface. A review of the piezoelectric coefficients $d_{13}$, $d_{33}$, and $d_{15}$ and polarization $P_{sp}$ was presented in Ref. 40. As the bandgap revision is not expected to affect these properties, we recommend the same values as recommended in Ref. 40 and list them in Table III. As a result of the piezoelectric and spontaneous polarization effects, a two-dimensional electron gas is expected to form on the interface of InN with InGaAlN alloys. Modeling of transport properties of such structures was performed by Hasan et al.,\textsuperscript{192} Kong et al.,\textsuperscript{193} and Yarar et al.\textsuperscript{194}

### 3. Phonon structures and dynamics

For the wurtzite structure, group theory predicts eight sets of normal phonon modes at the $\Gamma$ point, $\Gamma$ acoustic

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+ $\Gamma_{\text{optical}} = (A_1 + E_1) + (A_1 + 2B_1 + E_1 + 2E_2)$. The atomic displacement scheme of these phonon modes is depicted in Ref. 47. Among the six optical phonons, the two $E_2$ modes are only Raman active, the $A_1$ and $E_1$ modes are both Raman and IR active, and the two $B_1$ modes are neither Raman nor IR active (silent). For wurtzite film grown on (0001) substrate, only the $E_2$ and $A_1$(LO) modes are allowed by the polarization selection rules in backscattering geometry. This results in the fact that the $E_2$ and $A_1$(LO) modes are the best studied phonon modes in group-III nitrides. Figure 29(a) shows the phonon dispersion of wurtzite InN and the corresponding phonon density of states calculated by Davydov et al.\textsuperscript{48} The $E_2$ and $A_1$(LO) modes in InGaN alloys measured by Raman scattering spectroscopy have a linear dependence on the composition, as shown in Fig. 29(b) which contains experimental data measured by several groups.\textsuperscript{196,197} The phonon modes in InAlN alloys have not been thoroughly experimentally characterized. However, from the linear composition dependence of $A_1$(LO) and $E_2$ phonon energies in InGaN alloys, it is reasonable to assume that the phonon energies also interpolate linearly between InN and AlN. There is little controversy in the phonon energies in InN, GaN, and AlN. Recommended values are listed in Table I.

From Fig. 29(a) it can be seen that there exists a large phononic bandgap in InN. This is understandable given the fact that the atomic mass of In differs from that of $N$ by a factor of 8.2. A simple diatomic linear chain model (with heavy atomic mass $M$ and light atomic mass $m$) predicts a relative phononic bandgap of \textsuperscript{198}

$$\frac{\omega_{\text{optical}}^{\text{min}} - \omega_{\text{acoustic}}^{\text{max}}}{\omega_{\text{acoustic}}^{\text{min}}} = \sqrt{\frac{M}{m} - 1}, \quad (14a)$$

and a relative optical phonon band width of

$$\frac{\omega_{\text{optical}}^{\text{max}} - \omega_{\text{optical}}^{\text{min}}}{\omega_{\text{optical}}^{\text{max}}} = \sqrt{1 + \frac{m}{M} - 1}. \quad (14b)$$

Although this model overestimates the phononic bandgap and underestimates the phonon band width, the trend with $m/M$ is clear. InN is thus expected to have the widest phononic bandgap and the narrowest optical phonon band width among all group III-V semiconductors.

Such a wide phononic bandgap and narrow phonon band width present interesting opportunities for applications in hot-carrier solar cells. In such cells the thermalization of photoexcited carriers is slowed down to allow time for the carriers to be extracted while they are still “hot,” and thus achieving a high photovoltage.\textsuperscript{199} Hot carriers lose their energy by emitting optical phonons. The optical phonons then decay predominantly by two mechanisms: the Klemens process, where an optical phonon decays into two LA phonons with opposite momentum and energy of half that of the optical phonon;\textsuperscript{200} the Ridley process, where a LO phonon decays into a TO phonon and a LA phonon.\textsuperscript{201} In materials with large phononic bandgap between optical and acoustic phonons, the Klemens process is blocked; in materials with narrow optical phonon band width, the Ridley process is less likely. InN has a phonon structure that well fits these conditions. Therefore, hot carriers are expected to have a long lifetime in InN due to its beneficial phonon structure, a phenomenon known as the phonon bottleneck effect. In cubic InN is expected to be an even better choice as a hot-carrier absorber.\textsuperscript{202}

A relatively long hot-carrier lifetime has been reported in InN by Chen et al.\textsuperscript{203} Zanato et al.\textsuperscript{204} and Pacebutas et al.\textsuperscript{205} reported electron-phonon scattering time and optical bleaching effects in InN, respectively, both agreeing with a long hot-carrier lifetime. However, Sun et al.\textsuperscript{206} recently reported a shorter hot-carrier lifetime of $\sim$0.4 ps,\textsuperscript{205} and the same group argued that the plasma screening of electron-LO phonon interactions, rather than the hot phonon effect, is responsible for the slow energy loss rate.\textsuperscript{206} Optical phonon lifetimes on the order of approximately picoseconds have also been observed by Pomeroy et al. using Raman scattering spectroscopy.\textsuperscript{207} Ascazubi et al. reported that the hot-carrier thermalization was significantly accelerated when InN is doped with Si,\textsuperscript{91} an effect the authors attribute to Si-induced electronic states in the electronic bandgap; however, Conibeer et al. point out that a more likely explanation would be that Si introduces vibrational states into the phononic bandgap, and hence facilitates the Klemens mechanism.\textsuperscript{202} The possible slow hot-carrier thermalization combined with the tunable bandgap of In-rich InGaN alloys motivates studies for applications in high-efficiency solar cells.
cies using the multijunction concept, four or a greater num-

IV. NEW APPLICATIONS

The re-evaluation of the InN bandgap and subsequent findings have a significant impact on device applications of group-III nitrides. The bandgap of InGaN alloys ranging from 0.64 to 3.42 eV provides an almost perfect match to the solar spectrum, as shown in Fig. 30. This opens up an interesting opportunity for using these alloys in high-efficiency solar cells. The important wavelength 1.55 μm for fiber optics is just slightly higher in energy than the bandgap of InN, and therefore can be emitted by InN when alloyed with small fractions of GaN, stressed, quantum confined, or doped with high electron concentrations. The visible spectrum is well within the bandgap range of the InGaN alloys, offering a possibility to fabricate full-color light emitting devices with this single alloy system. The surface electron accumulation layer and small effective electron mass of InN also find applications in chemical sensing and fast electronics. In the following we summarize the state-of-the-art developments in these applications.

A. Photovoltaics

InN and InGaN have the following advantages for solar cell applications: (i) bandgap continuously tunable within the energy range of the solar spectrum; (ii) superior resistance against high-energy particle radiation, making them especially suitable for space applications; (iii) possible strong phonon bottleneck effect to slow down hot-carrier cooling; (iv) advantageous band alignment with respect to Si, so that a recombination junction naturally exists for cells using a Si base. Since it was first proposed to use InGaN for solar cell applications, 67 significant efforts and progress have been made toward this goal, while great opportunities and grand challenges coexist.

The maximum solar energy conversion efficiency (∼43%) is achieved in triple-junction cells based on three different semiconductors with fixed bandgaps and nearly matched lattice constant, Ge (0.7 eV), GaAs (1.4 eV), and GaInP (1.9 eV). In order to attain >50% conversion efficiencies using the multijunction concept, four or a greater number of junctions are needed. Finding materials with the required bandgap becomes a major challenge. For example, from detailed balance modeling, for an ideal four-junction solar cell that can reach 62% theoretical efficiency, a tandem of junctions with bandgaps of 0.6, 1.11, 1.69, and 2.48 eV is required. 208 The InGaN alloys would allow fine tuning in optimization of the performance of these cells by offering flexibility in the choice of the bandgaps. 209

For double-junction cells, the maximum theoretical efficiency is about 39% when two junctions with bandgaps of 1.1 and 1.75 eV are used. 210 Silicon has a bandgap of 1.1 eV, ideally suitable for the bottom junction. In1−xGaN has a bandgap of 1.75 eV when x = 0.5. Therefore, a tandem structure of p-In0.5Ga0.5N/n-In0.5Ga0.5N/p-Si/n-Si would form a high-efficiency double-junction cell. An additional benefit of this structure comes from the band alignment between InGaN and Si. 211 As shown in Fig. 21, at x = 0.5, the VBM of Si lines up with the CBM of In1−xGaN. Therefore, the n-In0.5Ga0.5N/p-Si interface would be a low-resistance Ohmic junction, acting as a natural "recombination junction" connecting the top and bottom cells. Heavy doping of the interface that is normally required for multijunction cells is not necessary in this cell. Using an analytical model developed by Kurtz et al., 210 Hsu and Walukiewicz calculated the theoretical efficiency of such a double-junction cell. They found that double-junction InGaN/Si solar cells can have significantly higher efficiencies than single-junction Si solar cells, with energy conversion efficiencies of more than 31% when high-quality materials are used [Fig. 31(a)]. For low-quality polycrystalline Si, adding an InGaN junction on top of Si can increase the efficiency by more than 50%, from 17% for Si alone to 27%. Such an increase in the efficiency could justify the cost increase associated with the complexity of growing these cells. Adding a second InGaN junction with an appropriate composition can provide further boosts to the efficiency. A three-junction In1−xGaN/Ni1−yGaN/Si solar cell could offer energy conversion efficiencies exceeding 35% [Fig. 31(b)].

Besides integrating on a Si junction to form a multijunction cell, InGaN can also be used for a single-junction solar cell that meets the 2.4 eV requirement in a lateral cell architecture. 212,213 In this design, solar cell arrays with different bandgaps are laid out laterally; the sunlight is dispersed by optics and focused separately onto these solar cells that best match the wavelengths, so that over 90% of the photons will land on the correct solar cells and maximize the

FIG. 30. (Color online) The bandgap of the group III-nitride alloys as a function of the a-axis lattice constant, compared to the visible colors, solar spectrum, and 1.55 μm wavelength.

FIG. 31. (a) Calculated efficiency of high-quality InGaN/Si two junction solar cells as a function of InGaN bandgap. The physical thickness of the Si junction is labeled for each curve. (b) Isoefficiency plot of an In1−xGaN/In1−yGaN/Si triple-junction solar cell as a function of the bandgaps of the two InGaN junctions. Reference 211.
total energy conversion. In addition, other exotic concepts such as graded-bandgap solar cells\textsuperscript{214} can also be explored with the InGaN system. We note that growth of graded-composition InGaN thin films has been demonstrated.\textsuperscript{215}

Fabrication of these cells faces major challenges, including lattice mismatch, $p$-type doping, phase separation, and surface states. In$_{1-x}$Ga$_x$N (0001) has a lattice mismatch with Si (111) between 8\% (when $x=0$) and 16\% (when $x=1$). InN films\textsuperscript{216–222} and nanowire arrays\textsuperscript{218,223,224} have been grown epitaxially on Si substrates using MBE or MOCVD.\textsuperscript{225–227} In order to achieve good film quality, a thin Si$_3$N$_4$ or AlN layer is typically used as a buffer. However, it is not clear whether these structures currently have materials quality suitable for high-performance photovoltaics. Similar issues need to be addressed in the In$_{1-x}$Ga$_x$N/In$_{1-y}$Ga$_y$N cell and graded-bandgap cell. $p$-type doping of InN and In-rich InGaN is still in the exploratory stage, and a $p$-$n$ junction has yet to be demonstrated. Nevertheless, fabrication of Ga-rich InGaN cells has been attempted by several groups.\textsuperscript{228–231} Figure 32 shows the structure and performance of a single-junction In$_{0.35}$Ga$_{0.72}$N solar cell grown by Jani \textit{et al.} using MOCVD.\textsuperscript{229} The high open-circuit voltage of 2.1 eV is consistent with the bandgap of In$_{0.25}$Ga$_{0.72}$N at 2.4 eV. This is the highest In composition in a $p$-$n$ junction that has been reported to show a strong photovoltaic response. Further increase in In composition leads to leaky junctions with poor photovoltaic performance as shown by Chen \textit{et al.}\textsuperscript{230} Phase separation in InGaN is detrimental to the device performance because it reduces the short-circuit current by generating recombination centers, and reduces the open-circuit voltage through bandgap fluctuations. In the work of Jani \textit{et al.}, the phase separation was controlled by increasing the indium carrier gas flow rate, increasing the growth rate and limiting the thickness of the epitaxy.\textsuperscript{229} The same group also reported the fabrication of $p$-Ga$N/i$-InGaN/$n$-GaN solar cells which show high open-circuit voltage and high internal quantum efficiency.\textsuperscript{232} Surface states in InN and In-rich InGaN tend to accumulate a high density of electrons over the depth of several nanometers from the surface, regardless of the bulk doping type (see Sec. III B). This surface electron layer prevents a direct Ohmic contact to $p$-type InGaN. No evidence has been shown that such a surface inversion layer on In-rich $p$-InGaN can be removed by passivating the surface states. Alternatively, it is possible to grade the composition of InGaN toward the surface, such that the surface composition becomes Ga-rich, making an Ohmic contact possible. However, the grading scheme has to be carefully designed so as not to block the majority carrier flow.

**B. Solid state lighting and 1.55 $\mu$m and terahertz emission**

The EQE of LEDs based on Ga-rich InGaN drops at the green wavelengths, which are, ironically, at the peak of the human eye response and a critical component of natural white lighting [Fig. 1(b)]. As a result, efficient full-visible-spectrum LEDs using a single materials system are not available. Solid state white lighting is currently achieved in a relatively inefficient way by combining blue InGaN LEDs with phosphor technology. Realizing high-EQE green and even red LEDs with InGaN is recognized as one of the major research challenges for solid state lighting.\textsuperscript{5} The inefficiency of green emission in InGaN is believed to arise from multiple effects. This includes spinodal decomposition of InGaN at high In contents, the piezoelectricity-induced quantum-confined Stark effect that spatially separates the electron and hole wave functions, and nonradiative recombination associated with native defects.\textsuperscript{233} Bright PL has been achieved in InGaN films over the entire spectral range from the bandgap of InN to that of GaN,\textsuperscript{61} as shown in Fig. 33(a). However, electrically driven InGaN light emitting devices require the formation of either a $p$-$n$ junction of InGaN, or $p$-$i$-$n$ quantum wells where InGaN is the active $i$ region and GaN is typically used as the barrier. The first approach faces the same obstacles as in solar cell applications, namely, $p$-type doping and Ohmic contacts. The second approach is challenged by the incompatibility of growth temperatures of InGaN and GaN layers, as InGaN tends to decompose at temperatures that are still too low to grow high-quality GaN. Nonetheless, recent advances in thin film deposition techniques enable the growth of InGaN-based multiple quantum well (MQW) LEDs with higher internal quantum efficiency. Figure 33(b) shows the emission spectra of In$_{0.03}$Ga$_{0.97}$N/GaN MQW LEDs fabricated by Xu \textit{et al.} using plasma-assisted MBE.\textsuperscript{234} The In fraction is 0.18, 0.41, and 0.46 for the blue, green, and red emitting devices, respectively. Green and longer-wavelength LEDs with similar structure based on InGaN have been reported by several groups.\textsuperscript{233,236–239} White LEDs based on multiple-color emission from InGaN LEDs have also been demonstrated.\textsuperscript{240,241} In these works the In fraction incorporated in InGaN is still less than but close to 0.5. With these rapid developments, there are plenty of reasons to believe that the "green valley
optical rectification. Comparing InN and InAs, Polyakov studied the terahertz emission in InN to resonance-enhanced optical rectification in films with composition covering the entire range 0 < x < 1. Reference 234.

The quest for brighter sources in terahertz spectroscopy and imaging has also placed InN into the focus of investigation for terahertz emission. The first demonstration of strong terahertz emission from narrow-gap InN was reported by Asacuzi et al.244 where the emission was attributed to optically excited transient photocurrents. Later Mattheaus et al. compared the terahertz emission of InN with other semiconductors and concluded that the emission mechanism is the photo-Dember effect that occurs as a result of different diffusion coefficients of electrons and holes.245 Mu et al. attributed the terahertz emission in InN to resonance-enhanced optical rectification.246 Comparing InN and InAs, Polyakov and Schwierz analyzed the importance of band structure in the terahertz emission efficiency. Very recently, Ahn et al. reported a significant enhancement in terahertz emission power from a-plane InN films, and explained the effect by the acceleration of photoexcited carriers under the polarization-induced in-plane electric field.248

C. Chemical sensors and field-effect transistors

The unusual band bending and electron accumulation near the surface of InN are being exploited for chemical sensing and field-effect devices. Soon after the discovery of the narrow bandgap of InN, Lu et al. reported a fast response of sheet carrier concentration and mobility to solvent exposures such as methanol and water.249 Pt-coated InN nanorods were found to change resistance upon exposure to H2 but not to N2 and O2.250 The InN surface has been functionalized by aminosilane molecules and used to bind negatively charged Au colloids.251 Anion sensing using InN with remarkable selectivity, stability, response time, and repeatability was shown by Lu et al.252,253 In these experiments InN is sensitive to anions but not cations, indicating that the sensing mechanism is based on positively charged surface states of InN attracting negatively charged ions in aqueous solutions.

High electron drift velocities in InN were reported by Tsen et al. using ultrafast Raman spectroscopy.172 The cutoff drift velocity at ∼2 × 106 cm/s is higher than that of other group III-V semiconductors. This is understood by the band structure of InN featuring a low electron effective mass at the Γ point and a large energy separation between the Γ point and satellite valleys. In light of these superior properties, Lin et al. fabricated the first field-effect transistors (FETs) based on InN/AlN heterojunctions.254 A standard transistor behavior was observed with a high source-drain current density that was attributed to the high sheet carrier density in a ultrathin InN layer. Hauguth-Frank et al. fabricated photodetectors using ultrathin In1−xGa,N (x < 0.44) layers.255 Lebedev reported that in ultrathin In1−xGa,N/GaN (x < 0.5) heterostructures, free electrons tend to accumulate at the buried InGaN/GaN interface instead of on the surface, and therefore the mobility is limited by the interface quality.256

V. GROUP III-NITRIDE NANOSTRUCTURES

In recent years, semiconductor nanostructures have come under extensive investigations for applications in high-performance electronic257,258 and optical259 devices. They offer a distinct way to study electrical, photonic, and thermal transport phenomena as a function of dimensionality, size reduction, and surface-to-volume ratio. In particular, a wide range of demonstrated and potential applications have made semiconductor nanowires (NWs) and quantum dots (QDs) a rapidly growing focus of research. With the interesting properties of InN and In-rich group-III nitrides described in previous sections, there has been much exploration into the growth and characterization of InN, In1−xGa,N, and In1−xAl,N nanostructures.

FIG. 33. (Color online) (a) Photoluminescence peak energy of In0.7Ga0.3N MQWs with different InN well thickness reported by Che et al.235 (b) Electroluminescence spectra of In0.7Ga0.3N/GaN MQW LEDs. The In fraction is 0.18, 0.41, and 0.46 for the blue, green and red emitting devices, respectively. Reference 234. (c) InN/In0.7Ga0.3N MQWs with different InN well widths emitting near 1.55 μm. Calculated dependence assuming different internal electric field is also shown. Reference 235.
A. InN nanostructures: Optical properties

InN NWs have been grown using low-temperature MBE and MOCVD. Figure 34 shows such an example. These InN NW arrays were grown epitaxially on Si (111) substrates by Calleja et al. using plasma-enhanced MBE. Under N-rich growth conditions InN tends to form such single-crystal NW arrays. Growth of InN nanostructures with various geometries, such as nanowires, nanorods, nanocolumns, nanotips, nanotubes, nanobelts, and nanocrystals, has been reported by numerous groups. Most of these studies showed a light emission consistent with the narrow bandgap near 0.7 eV.

Figure 35(a) shows the bandgap and PL intensity of InN NWs as a function of electron concentration \( n \) derived from fitting the PL line shape with a model that considers the electron and hole distributions in the nanowires. The PL intensity was found to scale as \( \sim n^{-2.6} \), a stronger dependence than that of the Auger recombination, for which a dependence of \( n^{-1} \) is expected. The authors thus conclude that the decrease in PL efficiency arises not only as a result of the increase in bulk electron concentration, but also because of increasing importance of nonradiative recombination processes, such as recombination at the nanowire surface possibly related to the intrinsic surface accumulation layer. The fundamental bandgap is reduced in this layer, an evidence of the bandgap renormalization effect. In nanowires these effects become more prominent due to the large surface-to-volume ratio. They are responsible for the decrease in \( E_g \) with increasing \( n \) in Fig. 35(a).

As in other semiconductor nanostructures, the optical bandgap of InN increases in the presence of substantial quantum confinement. The characteristic length scale for this to become significant is comparable to the exciton Bohr radius, which is on the order of 10 nm for InN. Chao et al. reported a blueshift of the PL spectra with decreasing InN nanorod diameters. The PL intensity depends linearly on the excitation power over two orders of magnitude (5–300 mW), indicating the interband transition nature of the luminescence. Similar blueshift in PL has been observed in InN quantum dots as well. Figure 35(c) shows the PL spectra of self-assembled InN QDs embedded in GaN grown by MOCVD. The QD height was measured by AFM, and determines the degree of confinement in the QDs. The peak energies shift systematically from 0.78 to 1.07 eV as the average dot height was reduced from 32.4 to 6.5 nm. The inset shows that the PL peak shift can be well explained by a standard quantum confinement model within the effective mass approximation.

Ultraviolet lasing has been achieved in ZnO nanowires where the faceted surfaces form natural resonance cavities. Similar lasing activities have been observed in InN nanobelts for infrared wavelengths. These InN nanobelts were grown by MOCVD along the [110] direction and were enclosed by \{001\} and \{110\} planes. As shown in Fig. 35(d), the nanobelts undergo a transition from spontaneous emission to stimulated emission when the excitation power is above a threshold. Sharp lasing peaks emerge on top of the broad spontaneous emission peak, where the lasing wavelengths are determined by the Fabry–Pérot cavity of the nanobelts.

B. InN nanostructures: Electronic properties

Electroluminescence (EL) is a powerful tool to probe the electron-photon interactions in single NWs in the field-effect transistor geometry where the nanowire is electrically biased between a source and a drain electrode. Spectrally resolved light emission is recorded as a function of the biasing voltage and back gate voltage. Chen et al. have performed such EL experiments on single InN NWs. The EL spectrum shows a peak near \( E_g \) of InN and blueshifts at higher temperature. The EL intensity increases with increasing biasing voltage \( V_d \) as \( \exp(-V_0/V_d) \), where \( V_0 \) is a parameter depending on the optical phonon scattering length in the NW. These observations agree well with an impact excitation mechanism. The surface accumulation layer was found to enhance the radia-
tive electron-hole recombination in these InN nanowires through a plasmon-exciton coupling mechanism.

FETs using InN NWs with diameters between 70 and 150 nm have been fabricated. The electron mobility in these devices was extracted by measuring the transconductance in response to a gate voltage. It was found that the mobility is comparable to bulk InN with similar doping. In similar experiments, the dependence of resistance on the nanowire diameter was found to deviate from simple geometric scaling, and attributed to stronger surface influence. Recently, Bloemers et al. measured the magnetoresistance of single InN nanowires at variable temperatures. Information on phase coherent transport is obtained by analyzing the characteristic fluctuation pattern in the magnetoresistance. The phase coherent length, which defines the nanowire length below which a phase coherent transport is maintained, was determined to be between 200–400 nm depending on temperature. The same group has reported magnetoresistance oscillations with a periodicity corresponding to a single magnetic flux quantum. The effect originates from the phase coherent transport in InN NWs with the unique cylindrical surface conduction geometry.

Other applications of InN nanostructures are also emerging. For example, Wang et al. reported excellent field emission properties from InN nanotips. The authors ascribed the superior properties to the intrinsic surface accumulation layer where the band is bent in a manner that the electron tunneling barrier is significantly reduced. Single-walled InN nanotubes were predicted to have the lowest curvature-induced strain energy compared to other group III-V and group IV nanotubes. Calculations show that they are all semiconductors with an almost constant bandgap of about 1 eV.

C. In-rich InGaN nanowires

Nanowire devices harnessing the wide-spectrum possibilities of group-III nitrides have only recently been developed at the laboratory scale. Multicolor LEDs, lasers, photoelectrodes, and high-mobility FETs (Ref. 294) have been demonstrated with Ga-rich InGaN and GaAlN NWs and NW heterostructures. In these NW devices the highest In content used was 0.35, corresponding to ~600 nm orange-color emission.

Recently Kuykendall et al. synthesized In$_{x}$Ga$_{1-x}$N NWs utilizing a combinatorial low-temperature halide CVD. X-ray and electron diffraction prove that these NWs were grown as single crystals over the entire composition range of 0 < $x$ < 1 across a single substrate without phase separation. It was argued that these NWs were grown via a self-catalyzed process enabled by the low growth temperature (550 °C) and high growth rate which stabilizes thermodynamically unstable product. Figure 36 shows the optical characterization of these NWs. Despite the strong "yellow luminescence" for Ga-rich compositions which is typical for Ga-rich InGaN thin films as well, these NWs exhibit bandgap values spanning from the infrared (1.2 eV) to the ultraviolet (3.4 eV) spectral range. This range is consistent with the narrow bandgap of InN, and shows great potential for fabricating nanoscale full-color light emitting and light harvesting devices. One of the remarkable properties of these NWs is the high quantum efficiency over a wide range of compositions. The authors suggest that this improvement is due to the unique growth mechanism and geometry of NWs; these help relax strain and eliminate threading dislocations, which usually act as nonradiative recombination centers in InGaN thin films.

VI. CONCLUSIONS AND OUTLOOKS

We have presented an up-to-date review of the physical properties and applications of InN and related group III-nitride alloys.

InN has the largest cation-anion electronegativity difference and atomic mass ratio among all group III-V semiconductors. As a consequence of these unique characteristics InN features an unusually low conduction band minimum and a wide phononic bandgap. Extraordinary materials properties thus arise in InN, including a nonparabolic conduction band, a small electron effective mass, intrinsic surface electron accumulation, strong background electron doping, high radiation resistance, and slowed hot phonon cooling. After the revision of the narrow bandgap of InN, fundamental band parameters of InN and In-rich InGaN and InAlN alloys have been re-evaluated and were summarized in this review.

The bandgaps of group III-nitride alloys continuously span a wide spectrum ranging from the near infrared to the ultraviolet. Significant impact is expected on device applications by the group-III nitrides. Most interestingly, the direct
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