CHAPTER 1

Introduction and Motivation

After a half century development, GaN-based light-emitting diodes (LEDs) are being used in our daily life, for example smart phone and television back lighting, automobile lamps, traffic signals, street lamps and architecture illumination. LEDs have also begun to share the world's general illumination market. However, to dominate the lighting market there are two major challenges: increasing performance and cutting down production costs. In recent years, three-dimensional core-shell GaN-based columnar LEDs have been considered as one of the candidates for prospective solid-state lighting because of their properties which provide the possibilities to overcome efficiency limitations, despite their efficiency being currently still lower than that of conventional layer LEDs.

1.1 Historical development of light-emitting diodes

The first light-emitting diode was invented in 1907 during an investigation of rectifying solid-state detectors using SiC crystals by Henry Joseph Round in New York [1]. The light was produced when current flowed through a contact of carborundum (SiC) and metal electrodes. This crystal-metal contact forms a rectifying Schottky contact.

In the mid 1920s the Russian extremely talented scientist Oleg Vladimirovich Lossev who had no academic qualifications discovered the LED independently [2]. He understood that non-thermal emission of LEDs is related to diode action, measured the current-voltage (I-V) characteristics of devices, studied the temperature dependence of emission, modulated the LED emission and used the Einstein's quantum theory to explain the LED behaviors which was called by him "inverse photo-electric effect".

Sadly, in 1942 he passed away of hunger at the age of 39 during the blockade of Leningrad.

The development of modern LED technology started in the early 1960s. After the successful fabrication of GaAs wafers which were used as substrates, four American research groups, namely Radio Corporation of America (RCA), General Electric (GE), International Business Machines Corporation (IBM) and Massachusetts Institute of Technology (MIT) almost simultaneously reported the infrared (870-980 nm) LEDs and lasers based on GaAs crystals in 1962 [3] [4] [5]. In the following 10 years, low-cost commercial GaAsP red LEDs[1] were produced, GaP red LEDs with co-doped active regions[2] were reported, high-brightness AlGaAs LEDs with red emission were developed and N doped GaP green LEDs[3] were achieved [6].

After the achievement of red and green LEDs, a bright blue LED was still required for creating a full color image. In 1968, GaN was chosen as a blue LED candidate and investigated by the RCA Laboratories. In 1969 the first single-crystalline GaN film was successfully deposited on sapphire [7]. The GaN films without intentional doping proved to be n-type, while conducting p-type was difficult to be achieved. Zn and Mg seemed to be appropriate acceptors, but Zn- and Mg-doped GaN films were insulating layers. Using an undoped n-type GaN layer, a Zn-doped insulating layer and an indium surface contact, the RCA team realized the first current-injected GaN green and blue emitting device in 1972 [8], which was not based on a p-n junction but instead on a metal-insulator-semiconductor (MIS) diode structure. Unfortunately, its efficiency was very low, and as a consequence, the work on GaN ceased.

1 GaAs has a direct band gap and GaP has a indirect band gap. When the phosphor concentration in GaAsP alloy exceeds 44%, a direct-indirect transition of band gap occurs, which leads to a strong decrease in the LED radiative efficiency.

2 In the co-doped active region of GaP LEDs, Zn can be used as acceptor and Te, S or Se can be used as donors, so that strong light emission is generated by donor-acceptor pair recombination processes and the energy of the emitted light is below the GaP band gap. The co-doped active regions was developed before the double heterojunction for LEDs.

3 GaP is an indirect-gap semiconductor with band gap of 2.25 eV 300 K, thus a phonon is required in optical transitions. Therefore, the first GaP p-n junction LEDs did not emit significant amounts of light. However, if GaP is doped with an optically active isoelectronic impurity such as N or O, strong optical transition in green and red parts of the spectrum are observed, respectively. It can be explained by **Heisenberg's uncertainty principle** ($\triangle x \triangle p > h/2\pi$), which predicts that an electron wave function localized in real space (small $\triangle x$) is delocalized in momentum space (large $\triangle p$), so that the momentum-conserving (vertical) transition is possible. This green LEDs have been applied, e.g. in dial pad illumination of telephones.

However, in Nagoya, Japan, Isamu Akasaki and his team did not give up. In 1986, Amano, a graduate student in Akasaki's group, significantly improved the quality of the single-crystal GaN layer epitaxially grown on sapphire, by using a thin AlN buffer layer [9]. In 1989, they achieved the first true p-type conductivity in GaN by treating a Mg-doped GaN film with low-energy electron beam irradiation (LEEDI) [10]. Two years later in 1991, a high-temperature post-growth anneal method to activate Mg dopants in GaN was demonstrated by Shuji Nakamura et al. [11] who were working at the Nichia Chemical Industries Corporation, Japan. Two months later, Nakamura et al. concluded via their studies that hydrogen attached to Mg deactivated Mg as an acceptor [12].[1] In 1993, Nichia commercialized the GaN LEDs with Si and Zn co-doped active region [14] and in the same year Nakamura et al. announced the first InGaN/AlGaN double-heterostructure LED[2] with an external quantum efficiency (EQE) of 2.7% at 20 mA [15]. In 1995, high-brightness InGaN blue, green and yellow LEDs with single quantum well (SQW) structures[3] were reported by Nakamura et al. and the EQEs of these three different color LEDs were 7.3%, 2.1% and 0.5%, respectively [16]. This means that the InGaN/GaN material system is appropriate for full color or white LEDs.

After two decades of efforts, material quality and device fabrication of GaN-based LEDs have been steadily improved. In 2013 Cree, Inc. set a new R&D[4] performance record with 276 lumens per watt (lm/W) [5] white LED in lab [17]. In the same year,

1 In the earlier studies, it was well established that hydrogen passivates (neutralizes) shallow donors and acceptors in III-V material and Si, e.g. the hole concentration in Zn-doped p-type GaAs was strongly reduced by the formation of Zn-H neutral complexes, and reactivation of the acceptors can be realized by using thermal annealing [13].

2 The double-heterostructure structure consisted of 150 nm Si-doped $Al_{0.15}Ga_{0.85}N$, 50 nm Zn-doped $In_{0.06}Ga_{0.94}N$ and 150 nm p-doped $Al_{0.15}Ga_{0.85}N$.

3 The InGaN active layer was 2 nm thick and the the indium mole fraction was varied between 0.2 and 0.7 in oder to change the wavelength from blue to yellow.

4 Research and Development

5 The **lumen** is the unit of luminous flux, measuring the total emitted visible light from a source and respecting the sensitivity of the human eye to different light wavelengths. Luminous flux can be written as $\Phi_v = K_m \int_{380nm}^{780nm} V(\lambda) \frac{d\Phi_e(\lambda)}{d\lambda} d\lambda$, where $\frac{d}{d\lambda}\Phi_e(\lambda)$ is radiant flux per wavelength (the radiant flux Φ_e is given by $\Phi_e = N/t \cdot h \cdot f$, where N is the number of photo, t is the time, h is Planck constant and f is the frequency of the light), $V(\lambda)$ is dimensionless luminosity function describing the average spectral sensitivity of human visual perception of brightness, K_m is maximum photometric radiation equivalent with a value of 683 lm/W for daytime. lm/W is the unit of **luminous efficacy**, which is a measure of how well a light source produces visible light and is a ratio of luminous flux to power.

OSRAM has achieved 150 lm/W white LED for portable devices [18] and Philips developed an 200 lm/W warm white LED bulb (prototype) [19].

1.2 Current state of GaN-based solid-state lighting

Presently, the efficiency of commercial LED bulbs is 50-150 lm/W with a lifetime of about 30000-50000 h and the typical market price is generally higher than 20 $/klm [21]. In order to penetrate and finally dominate the general lighting market, LEDs should substitute the conventional bulbs, halogen lamps, fluorescent lamps (efficiency of 50-70 lm/W, lifetime of about 15000 h and price of about 2-10 $/klm [21]) and sodium-vapor lamps which are normally applied for the outdoor lighting, such as street lamps (efficiency of 100-150 lm/W, lifetime of 16000-30000 h and price of about 10 $/klm [22]). The development of different light sources are shown in Fig. 1.1.

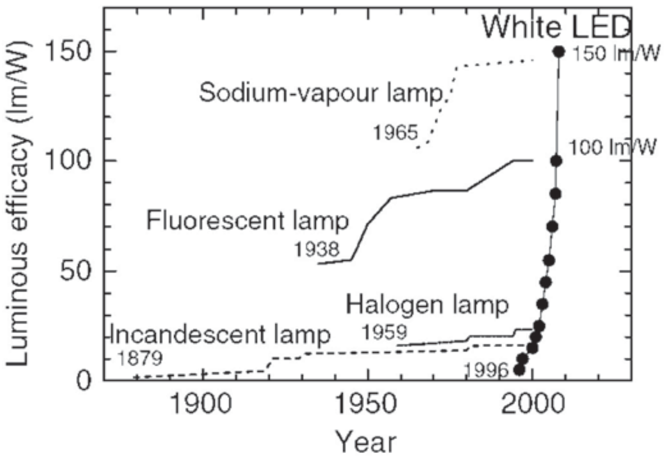

Figure 1.1: The history of luminous efficacy in incandescent lamps, halogen lamps, fluorescent lamps, sodium-vapour lamps and commercial white LEDs. The development years of white light sources are also shown. [20]

The theoretical limits to luminous efficacy of a white light source are calculated in the range 250 - 370 lm/W [23].[1] Thus, the challenges to further improve LEDs still remain, which will be discussed in the following paragraphs.

1 The maximum luminous efficacy is dependent on photopic sensitivity threshold, color temperature and color rendering index. The maximal luminous efficacy is 369 lm/W for a truncated black-body (422 - 647 nm) for a photopic sensitivity of 6.7% and the CRI of 87.4 at 2800 K. The maximal luminous efficacy decreases to 250 lm/W, when the photopic sensitivity threshold is reduced to 0.5%. The general maximal luminous efficacy is at about 330 lm/W.

1.2.1 Light extraction

Light extraction efficiency is one of the constraints of the LED efficiency. Prior to the discussion of light extraction efficiency, internal quantum efficiency (IQE) and external quantum efficiency (EQE) of LEDs should be introduced.

IQE is a very important metric of LEDs. It is a function of the quality of materials and structures. IQE can be defined as the fraction of the total current that feeds the radiative recombination inside the QW:

$$\eta_{IQE} = \frac{I_{rad}}{I_{total}} = \frac{I_{rad}}{I_{rad} + I_{lost}} = \frac{I_{rad}}{I_{rad} + I_{SRH} + I_{Auger} + I_{leak}} \tag{1.1}$$

where I_{total} is the total current of the device that feeds the radiative recombination inside the QW, I_{rad} is its part of carriers that generates photons inside the QWs, I_{SRH} is the current that derives defect-related Shockley-Read-Hall (SRH) non-radiative recombination inside the QWs, I_{Auger} is the non-radiative Auger recombination part of the current inside the QWs and I_{leak} is the leakage current of carriers that recombine outside the QWs [24]. Typical non-radiative electron-hole recombination at crystal defects is described by the SRH mode. The simple ABC model for carrier recombination inside the QW is

$$I_{QW} = I_{SRH} + I_{rad} + I_{Auger} = qV_{QW}(An + Bn^2 + Cn^3), \tag{1.2}$$

with the electron charge q, the active volume V_{QW} of all QWs, the carrier density inside the QW n, the SRH parameter A, the radiative coefficient B, and the Auger coefficient C. This means that the the defect-related non-radiative recombination is proportional to the dislocation density (the SRH parameter A), carrier density n and the active volume V_{QW}. The relationship between the leakage current I_{leak} and the current I_{QW} injected into the QWs is $I_{leak} = aI_{QW}^m$, where a and m are fit parameters.

Light extraction efficiency (η_{extr}) is one of the constraints of external quantum efficiency (η_{EQE}), which is given by the product of internal quantum efficiency (η_{IQE}) and light extraction efficiency (η_{extr}).

$$\eta_{EQE} = \eta_{IQE} \cdot \eta_{extr}. \tag{1.3}$$

The light extraction efficiency is mainly affected by the internal total reflection in conventional layer LEDs. The critical angle of the light extraction in GaN layer is about 23°, thus the fraction of light that can escape is about 4% [1] [25]. To improve the light extraction efficiency, many approaches have been reported, e.g. patterned substrate, surface texturation, using epoxy lens and chip shaping [26]. Recently, with optimized designs OSRAM can reach more than 80% light extraction efficiency [27]. Soraa Inc. developed a bulk GaN based triangular prisma fashion LED[2], its light extraction efficiency is close to 90%. Nowadays, the light extraction efficiency of commercial LEDs (blue light) normally lies in the range of 50-80% and their EQE lies in the range of 35-65%.

The overall power conversion efficiency of a LED is described by the wall-plug efficiency (η_{WPE}), which is given by the ratio of radiant flux with respect to electrical input power:

$$\eta_{WPE} = \frac{emitted\ \ flux\ \ [W]}{electrical\ \ input\ \ power\ \ [W]} = \eta_{el} \cdot \eta_{IQE} \cdot \eta_{extr} \cdot \eta_{pack} \cdot \eta_{conv} \cdot \eta_{St}, \qquad (1.4)$$

with the electrical efficiency η_{el}[3], internal quantum efficiency η_{IQE}, light extraction efficiency η_{extr}, package efficiency η_{pack}[4], conversion efficiency η_{conv}[5] and the Stokes losses η_{St}[6].

Increasing the light extraction efficiency η_{extr} and η_{IQE} is the most efficient approach to improve the wall-plug efficiency. It is because based on Eq. 1.4, η_{St} is a constant value; the room for improvement of η_{el}, η_{pack} and η_{conv} is very small. Until 2013, the η_{WPE} of commercial LEDs was in the range of 25-45%.

1 The refractive index of GaN is 2.5 for 460 nm wave length. The fraction of the light emitted inside a semiconductor which can escape from the semiconductor is given $\frac{P_{escape}}{P_{source}} = \frac{1}{2}(1 - cos\phi_c)$. ϕ_c is the critical angle for total reflection.

2 This chip employs both the geometric shaping and a textured top surface. The in-plane light extracts after only one or two bounces in the LED.

3 Ohmic losses owing to the resistance of epitaxial layers and contacts imply an electrical efficiency smaller than 1. Normally the η_{el} can reach up to 90%.

4 η_{pack} can reach up to 95%.

5 The efficiency of the conversion of blue light to yellow light using phosphor, which is typically higher than 90%.

6 The Stokes loss is given by the ratio of the mismatch in energy between, e.g. the blue and the yellow light. In this case, $\eta_{St} \approx 81\%$.

1.2.2 Dislocations

Until now, all commercial GaN-based LEDs are grown on foreign substrates, e.g. sapphire, silicon carbide and silicon, because a freestanding GaN substrate with high-quality, large area and low-cost is not available. However, the use of foreign substrates results in a high density of dislocations in the range of 10^7 - 10^9 cm^{-2} in common GaN layer due to lattice and thermal mismatches between GaN and substrates [28].

Non-radiative electron-hole recombination at crystal dislocations inside the QWs leads to a detriment of the η_{IQE} of LEDs. This has been described by the SRH model [29]. Sustaining a dislocation density of about 10^8 cm^{-2}, the η_{IQE} of commercial blue LEDs can reach about 80% [30]. Reducing the dislocation density can improve the IQE. Using bulk GaN substrates with a dislocation density of 10^6 cm^{-2}, the η_{IQE} of the blue LEDs exceeded 90% [31]. Besides, the leakage current is closely related to the density of dislocations. The reverse leakage current of LEDs decreases with an increasing density of screw dislocations in a GaN layer [32].

1.2.3 Quantum-confined Stark effect

It has been observed that the emission of c-plane GaN-based LEDs has a red shift, when the thickness of active layers increases. This effect is now understood as the quantum-confined Stark effect (QCSE). The QCSE describes that electron and hole wave functions are spatially separated in a QW when an external electric field is applied. In a polar-oriented InGaN/GaN QW structure, due to the lattice mismatch between GaN and InGaN the strain-induced piezoelectric field shifts the electron states to lower energies, while the hole states to higher energies. This decreases their wave function overlap and reduces the recombination probability.

The QCSE in GaN-based LEDs can be reduced by screening the piezoelectric field with injecting carriers or by Si-doping in quantum barriers (QBs) to cause a positive curvature of the QB band edge (cf. Fig. 1.2) [34]. To further eliminate or suppress the QCSE, nonpolar- and semipolar-oriented GaN LEDs grown on freestanding GaN and foreign substrates have been intensively investigated. For nonpolar LEDs, the polarization vectors lie in the plane, and thus no strain-induced electric fields appear in the device direction. Semipolar orientations can provide the effect of reduced strain-induced electric fields in the device direction. The $(20\bar{2}\bar{1})$ plane is considered as a promising candidate for semipolar LEDs, since the polarization related electric field

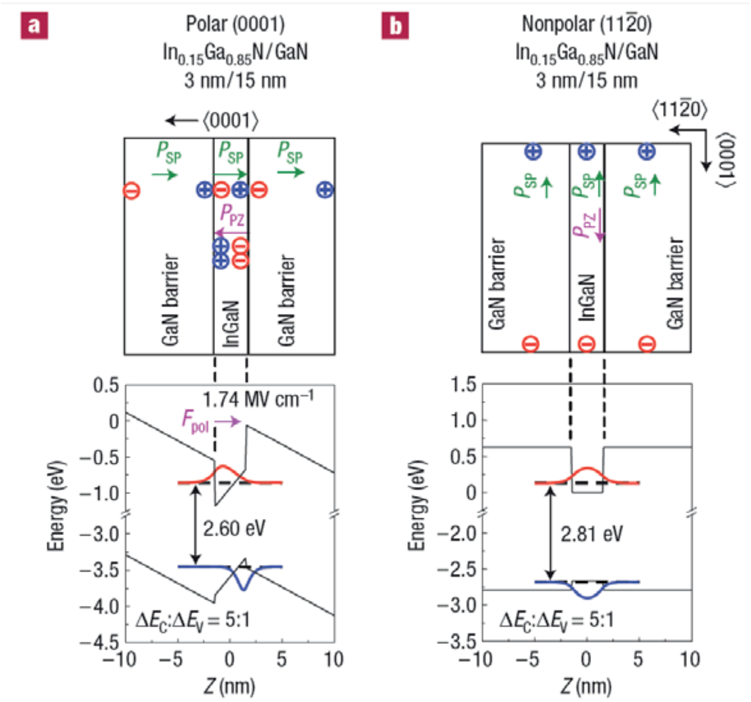

Figure 1.2: Schematic representation for polarizations and energy band profiles of strained $In_{0.15}Ga_{0.85}N/GaN$ quantum wells. (a) In polar Ga-face (0001) material, negative and positive immobile spontaneous polarization (P_{SP}) charges appear at surfaces and interfaces respectively. Because the InGaN QW is compressively strained, piezoelectric polarization (P_{PZ}) charges with an opposite sign to P_{SP} also appear at the respective interfaces. The resultant polarization is generally dominated by P_{PZ}, which induces the internal polarization field (F_{pol}) that points from the top interface (left) to the bottom interface (right). Consequently, the QW band profile is inclined (QCSE). (b) In nonpolar planes InGaN QWs, (F_{pol}) is parallel to the QW plane and the QWs do not experience QCSE. [33]

and the p-n junction built-in electric field are opposite in direction and nearly equal in magnitude [35].

1.2.4 Efficiency droop

In conventional GaN-based c-plane LEDs, the EQE reaches its maximum value at very low current densities, such as a few A·cm^{-2}, and monotonically decreases with the further increasing current density (cf. Fig. 1.3). This phenomenon is known as efficiency droop, which is the critical limitation for the usage of LEDs in high power application. At an elevated current density, such as 100 A·cm^{-2}, commercial blue LEDs exhibit in average 40%-50% efficiency droop and the best ones show 25%

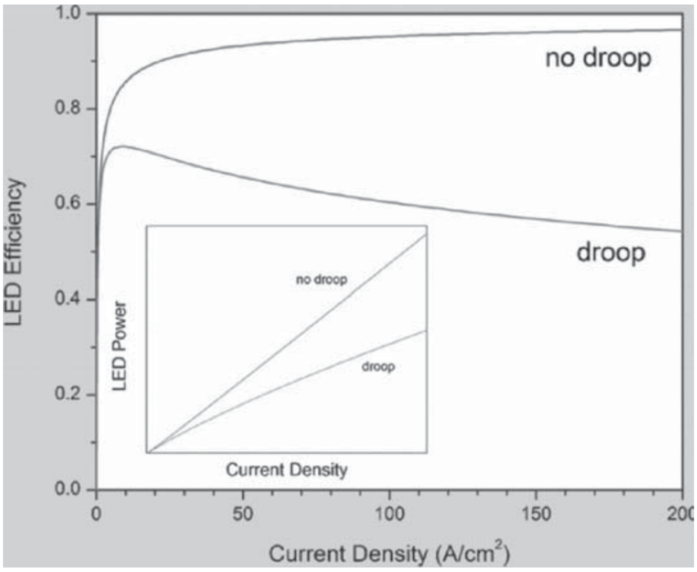

Figure 1.3: Illustration of LED efficiency droop (simulated). [24]

[36]. So far, the cause of the efficiency droop is still not fully understood. Many droop mechanisms are proposed, for instance, enhanced Auger recombination [37] and electron leakage [38] [39].

To improve the efficiency at high drive currents, a reduction of carrier density in active volumes is very efficient [40] [41]. The emission characteristics of a InGaN-based LED over a wide current-density range are shown in Fig. 1.4. The dominating recombination processes are strongly dependent on the current density. Based on the ABC model, carrier recombination inside the QW is describet by Eq. 1.2, where radiative recombination $I_{rad} \propto n^2$ and Auger recombination $I_{Auger} \propto n^3$ (SRH recombination does not cause efficiency droop [24]). Therefore, at a high current density Auger recombination is a culprit for the efficiency droop (orange line in Fig. 1.4). With a decreasing carrier density, the Auger recombination decreases much faster than the radiative recombination. Thus, at a lower current density (green line in Fig. 1.4) the radiative recombination dominants the processes. Therefore, the droop effect can be reduced by using a smaller current density. To reduce the current density there are several approaches, e.g. increasing the chip size, increasing the QW thickness and using the core-shell geometry.

Besides, an implementation of an AlGaN electron blocking layer (EBL) on the p-type side of MQW is a typical method to reduce the effect of electron leakage in GaN-based LEDs [24].

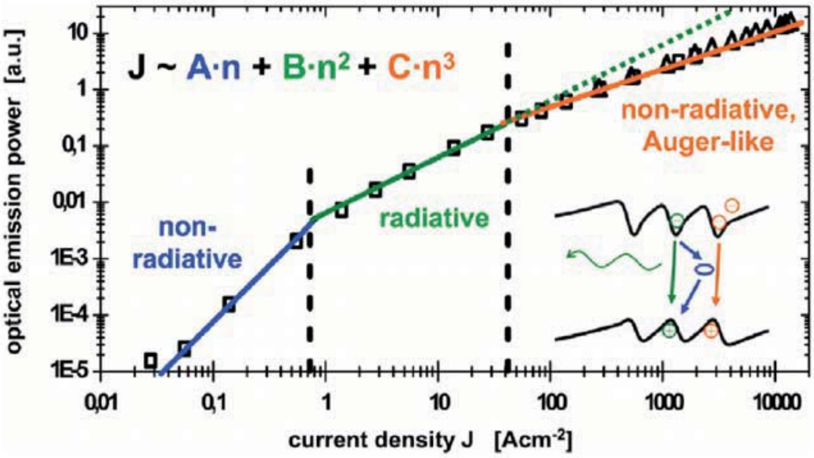

Figure 1.4: Emission power versus current density for a green-emitting multi-QW (MQW) LED. Different slopes can be attributed to different terms dominating the recombination-rate equation (e.g., solid blue, green, and orange lines). The corresponding recombination processes are shown in the band-diagram inset using the same colors. [41]

Otherwise, non-polar and semipolar LEDs are demonstrated as candidates for low droop LEDs, but the reduction of the efficiency droop is not significant [42] [43]. Due to the absence or reduction of QCSE on non-polar and semipolar facets, the overlap of electron- and hole-wave functions is improved, leading to an increased radiative recombination rate. However, radiative recombination ($I_{rad} \propto n^2$) is in competition with Auger recombination ($I_{Auger} \propto n^3$). Thus, the Auger recombination is also enhanced by the absence or reduction of QCSE. This could be the explanation for that the m-plane LEDs do not show a significant reduction of efficiency droop.

1.2.5 Green gap

Solid-state LEDs and laser diodes emitting in the range of about 520-635 nm have significantly declining efficiencies which is known as the "green gap" (cf. Fig. 1.5). The origin of this "green gap" phenomenon is still not fully understood.

For the long-wavelength LED materials, GaAsP is lattice mismatched to GaAs templates, and thus has many dislocations and is not suit for high-efficiency LEDs; GaP:N relies on deep-level-mediated transitions resulting in a saturation of radiative recombination at high injection-current levels; AlGaAs is a high-efficiency material for infrared and red LEDs, but it is unsuitable for orange and shorter wavelengths, because