Review

Photon management of GaN-based optoelectronic devices via nanoscaled phenomena


Abstract

Photon management is essential in improving the performances of optoelectronic devices including light emitting diodes, solar cells and photo detectors. Beyond the advances in material growth and device structure design, photon management via nanoscaled phenomena have also been demonstrated as a promising way for further modifying/improving the device performance. The accomplishments achieved by photon management via nanoscaled phenomena include strain-induced polarization field management, crystal quality improvement, light extraction/harvesting enhancement, radiation pattern control, and spectrum management. In this review, we summarize recent development, challenges and underlying physics of photon management in GaN-based light emitting diodes and solar cells.

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*Corresponding authors.
E-mail addresses: KYLAI@ncu.edu.tw (K.-Y. Lai), boon.ooi@kaust.edu.sa (B.S. Ooi), hckuo@faculty.nctu.edu.tw (H.-C. Kuo), jrhau.he@kaust.edu.sa (J.-H. He).

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1. Introduction

III-nitride materials have attracted great attention over the past decades. The bandgaps of the III-nitrides including AlN, GaN, InN materials and their related binary, ternary and quaternary compounds span 0.7 to 6.2 eV, which contribute to the emission/absorption ranging from deep ultraviolet (UV) to near infrared (NIR) region. Such large bandgap tunability, high thermal stability, direct bandgap make III-N materials the promising candidate for optoelectronic devices, such as light emitting diodes (LEDs), laser diodes (LDs) and solar cells [1–3]. Various applications such as full color displays, high density optical storage, automobile lights, visible light communication (VLC), biotechnology, and photovoltaic devices are vigorously developed.

However, the GaN-based devices are still obstructed by several issues, including low light extraction/harvesting, high defect density and strain-induced polarization [4–8]. To address these issues, there have been numerous approaches proposed over the past years. Fig. 1 shows the timeline of technology progresses in GaN optoelectronic devices. At early stages, the main efforts were focused on improving material qualities [9,10] and device structuring [11–13]. As time passes, the advanced growth/fabrication techniques enable photon management in nanostructured interfaces, further enhancing the quantum efficiencies of devices. For the
materials in low-dimension scale, many distinctive phenomena, e.g. reflection suppressing, scattering increase, strain reduction, can be observed in the optoelectronic devices with superior performances [14–18]. In the following sections, the photon management via nanoscaled phenomena in GaN-based LEDs and solar cells will be reviewed and discussed in details.

2. GaN technology overview

Tracing back to the development of GaN-based optoelectronic devices, the first milestone was achieved in 1969 by Maruska and Tietjen who utilized the hydride vapor-phase epitaxy to deposit polycrystalline-GaN on a foreign substrate (sapphire) [19]. Since then, several breakthroughs were made in the growth of single-crystalline GaN and InGaN, controlled p-type doping of GaN and epitaxial structures of LEDs and LDs [20]. The advancement in growth technology leads to the demonstration of candela-class high-brightness blue LEDs in 1993 [21,22]. These high-brightness c-plane blue LEDs grown on foreign substrates (e.g., sapphire, silicon carbide) have been successfully commercialized and used in a variety of applications including mobile displays, traffic signaling and flat panel displays. The demonstration of GaN-based high brightness white LEDs leads to extensive interest in the development of GaN-based solar cells in light of its wide-ranging bandgap energies, which holds the promise of nearly full absorption of solar spectrum [23,24].

3. Overview and challenges

3.1. LEDs overview and challenges

In general, the performance of LEDs is characterized by external quantum efficiency (EQE), which is defined as number of photons emitted per number of injected electrons. EQE is directly proportional to internal quantum efficiency (IQE) and the light extraction efficiency (LEE): \( EQE = IQE \times LEE \). In GaN-based LEDs, the IQE is directly related to the crystal quality of the epi-layer and the strain-induced polarization [25–27], while LEE is directly related to the large refractive index at the interface of GaN/air and GaN/substrate [28–30]. In this section, the issues affecting LED's efficiencies will be discussed.
3.1.1. Issues with IQE

The low IQE in GaN-based LEDs is mainly attributed to the high threading dislocation (TDs) density ($1 \times 10^8$–$1 \times 10^{12}$ cm$^{-2}$) due to the lack of native substrates for GaN/InGaN growth [31,32]. Sapphire is the most common substrate for GaN growth, however, there is a 13% lattice mismatch between c-plane sapphire and GaN [33,34]. This leads to high-density TDs stretching from the nucleation layer, which serves not only as non-radiative recombination centers but also the leakage current path, both reduce the IQE [35–37]. In addition to the low crystal qualities, the large internal electric fields induced by spontaneous and piezoelectric polarization also degrade the IQE of GaN-based LEDs. C-plane grown GaN-based LEDs strongly suffer from quantum confine Stark effect (QCSE), which is due to the piezoelectric field in strained Wurtzite InGaN/GaN multiple quantum wells (MQWs) and thus leads to spatial separation of the electron and hole wave functions [38–40]. The QCSE becomes even more severe for the MQW with high indium contents (>30%), which are required for the emitters in the green regime ($\lambda > 520$ nm) [41,42]. This efficiency droop of green LEDs, as known as the “green gap”, limits the development of high efficiency green LEDs [43–46]. Moreover, it is also very important to integrate the III-nitride epilayers with the well-developed Si technology in order to realize low cost, larger area and high thermal conductivity LEDs. However, the huge mismatch in lattice constant and thermal expansion coefficient between GaN and Si makes it challenging to achieve high efficiency LEDs on Si substrates [47,48].

3.1.2. Issues with light extraction efficiency

Even after a decade of commercialization, light extraction efficiencies (LEE) of GaN-based LEDs are still severely limited by the total internal reflection at air/GaN ($n = 2.43$) or air/ITO ($n = 2.06$) interfaces. The various photon paths accessible in lateral-type GaN-based LEDs are presented in Fig. 2. Recent numerical simulation results showed that at least 72% of the light emitted from InGaN quantum wells was confined in the epilayer, and 22% was transmitted to the sapphire substrate, indicating merely 6% of the light escaped out of the planar LEDs [49]. Most of the trapped photons in the device are reabsorbed by MQWs and eventually generates heat, degrading the IQE [50]. Moreover, after suffering multiple internal reflection within the LEDs, the photons were extracted towards the periphery of LEDs and emitted laterally, resulting in a larger view angle which severely limit the performances in some particular applications [51].

![Fig. 2. The light propagation and extraction in GaN-based LEDs.](image-url)
3.2. Solar cell overview and challenges

3.2.1. Issues with internal quantum efficiency

The low IQE of GaN-based solar cells can be attributed to the low crystal quality and strain-induced polarization field [52–54]. Similar to GaN-based LEDs, the TDs due to lattice mismatch between GaN and sapphire increase the non-recombination rate of photo-generated electron-hole pairs, and thus degrade the efficiency of GaN-based solar cells [55,56]. In addition, to maximize the efficiencies of GaN-based solar cells, a higher indium composition InGaN absorber is needed to extend its absorption wavelengths towards the long wavelength region (>550 nm) [57]. Unfortunately, it is well-known that InGaN layers with high indium contents will have to be grown at a relatively low temperature to increase indium incorporation, which often degrades the crystal quality [58]. Moreover, during the epitaxial growth of c-plane InGaN-based solar cells, the inherent spontaneous and strain-induced piezoelectric fields decrease the built-in field across the absorber, adversely affecting photo-current generation. The problem become even worse in the InGaN layers of increased indium content. Therefore the efficiencies of InGaN-based solar cells are currently not comparable to the devices made from other III–V compounds [59,60].

3.2.2. Issues with photon absorption

For solar cells, the antireflection and light trapping are very important for photon harvesting. As mentioned previously, the high-density TDs limit the IQE of GaN-based solar cells. To improve the crystal quality in the InGaN absorber, particularly for the case of high indium contents, InGaN (MQWs) with well thickness below 5 nm was commonly employed in the active region [61–63]. However, the efficiencies of InGaN-based MQW solar cells are still not satisfactory [64,65]. One of the reasons can be the high refractive index of GaN (n ≈ 2.5) that results in intensive reflection at air/device interface. Although the severe surface reflection is mitigated after coating with the transparent conducting oxide (e.g. ITO) and the passivation layer (e.g. SiO2), the AR performances of these layered structures are limited to particular wavelengths and narrow incident angles, which is an important issue for maximum light harvesting under the broad-band and omnidirectional solar illumination.

Fig. 3. Various nanostructuring techniques developed in last few years to enhance the efficiencies of LEDs.
4. Enhanced performance of GaN-based LEDs via nanoscaled phenomena

As discussed in previous sections, light output of LEDs is limited by insufficient light extraction and internal quantum efficiencies. To overcome these issues, different approaches for nanostructured LEDs were developed. Fig. 3 summarizes the techniques reported in the past decades, including nano-patterned substrates [66], surface nanotextures [67], nanorod LEDs [68], surface plasmon resonance [69], etc. The fabrication schemes and device performances of these techniques will be reviewed in this section.

4.1. Enhanced performance of GaN-based LEDs by surface engineering

It has been shown that a considerable amount of light emitted from the MQWs is trapped by the total internal reflection at the GaN/air interface, whereat large refractive index difference occurs and results in a small critical angle of $\sim 23^\circ$ [70,71]. The trapped light is eventually reabsorbed by MQWs and converted to heat [72,73]. The process significantly deteriorates the LEE and durability of the device. Therefore, breaking the TIR at LED surface is a key to enhance LEE. LEDs with micro-scale surface roughness have been demonstrated as an effective approach for enhancing LEE due to the increased probability of light escaping from LEDs through multiple reflection in the micro-scale structure [74,75]. As fabrication techniques advance, surface engineering with subwavelength dimensions was proposed as another strategy for further enhancing the photon extraction [50]. According to the effective refractive index theory, if the periodic of dielectric structure is comparable with the optical wavelength, the refractive index of dielectric structure can be replaced by an effective value, whose magnitude varies with the local volume ratio of the dielectric material to air [76]. As a result, the refractive index is gradually changed from the device to air, further alleviating the undesired TIR. Moreover, the nanostructured surface also induces strong scattering and thus results in an increased light-escaping cone [50]. In this section, the progress of surface engineering to enhance photon extraction of GaN-based LEDs is reviewed.

4.1.1. Roughening on p-GaN

There have been many reports on the methods of micro-/nano-roughening p-type GaN for LEE improvement, such as nano-imprinting lithography, or the masking processes utilizing self-assembly polystyrene nanospheres or metal nanoparticles [77–81]. These roughened surfaces were shown on the LEDs with greatly improved LEE. Moreover, a photoelectrochemical (PEC) etching method was also applied to the roughening of N-face GaN surfaces, which resulted in enhanced photon scattering and thus light extraction at the front side of the device [82]. Optimally roughened surface LED can lead to a two-fold to three-fold increase of LED output power. Many of these techniques have been commercialized lately. Researchers have also roughened both the u-GaN and p-GaN, termed as double roughening, and shown a 2.77-fold increase in LEE as compared with that of the conventional LEDs [83]. A more advanced strategy employing hierarchical structures combining p-GaN microdome and SiO$_2$ nanorod on LED surface was reported by Ho et al., as shown in Fig. 4 [84]. The hierarchical micro/nanoscale architecture was found to enhance the light output of blue LEDs by up to 36.8%. The mechanism of enhanced LEE is attributed to the multiple reflections in the microdome and additional graded refractive index profile provided by SiO$_2$ nanorods. One should note that roughening the GaN surface, if not performed properly, can sacrifice the electronic characteristics of LEDs because of
the surface defects induced by the dry etching. The degraded electronic properties often lead to high leakage currents and thus decreased reliability.

Compared with those mentioned above, photonic crystal is an even more advanced surface structuring strategy. The artificial structure is filled with periodically alternating refractive indices, forming a desirable "photonic band gap", with which light propagation within the structure can be effectively harnessed [85–87]. For the LEDs with properly designed photonic crystals, the light trapped by total internal reflection can be redirected into the radiative modes, which would greatly enhance LEE. In addition to the enhanced LEE, photonic crystals also yield the benefits of increased control over emission directionality and preserved light polarization [85], which are strongly desired in the applications of display, projectors, etc. However, since the technique requires wavelength-scale positioning of the media with different refractive indices, experimental demonstration of photonic crystal LEDs was not found until the nano-fabrication facilities become available. The first electrically driven photonic crystal LED was reported by Wierer et al. in 2004 [88], who employed electron-beam lithography to pattern the 190-nm n-GaN grown on the full device structure. The additionally grown n-GaN imparted a challenge faced by photonic crystal fabrication, i.e. the trade-off between light extraction and current spreading. In a typical nitride LED, perforating the resistive p-GaN window layer would further degrade the poor current spreading over MQWs. Although the resistance can be reduced with a thicker p-GaN, the increased thickness can result in excessive optical absorption from the MQWs. The issue can be tackled with the technologies of thin film fabrication [86,87] or embedded photonic crystals [87], in which periodic nanostructure is built on the less resistive n-GaN layer. The increased free carrier
concentration in n-GaN makes the layer more immune to the conductance-sacrificing fabrication. Moreover, these two technologies can further extract the low order guided modes thanks to the improved coupling efficiencies between the MQW and the photonic crystals [87].

4.1.2. Dielectric nano-structure on p-GaN

Inserting a dielectric material with the refractive index between GaN ($n = 2.5$) and air ($n = 1$) is a simple, and effective approach to improve LEE without degrading electrical performances of the device. Nanostructured oxides with refractive indices between those of GaN and air, e.g. SiO$_2$, ZnO, and ITO, with different geometry have been utilized to extract the trapped photons. In 2007, Ee et al., reported that InGaIn/GaN MQW LEDs structure utilizing a SiO$_2$/polystyrene lens array, resulting in significant enhancement of the LEE from the top surface of the LEDs [89]. The SiO$_2$/PS spheres attained via rapid convective deposition led to a 219% improvement of output power at the driving current of 100 mA [89]. Young-Min Song et al. directly fabricated sub-wavelength textures on the indium-tin-oxide (ITO) transparent conducting layer by dry etching with Ag nanoparticles as the mask, and showed 30.2% improvement in light output power, without degrading the electrical properties [90]. The enhanced LEE is mainly attributed to the increase in the effective photon escape cone and reduced internal Fresnel reflection.

Although the LEE can be effectively boosted by random surface roughening, harnessing the directionality of light emission requires additional experimental schemes. Directional emission can be controlled by dielectric nanorods with a waveguide effect. Hsiao et al. fabricated the syringe-like ZnO nanorods on the LED surface by hydrothermal method to enhance the LEE and to control the directional emission of LEDs, shown in Fig. 5 [91]. With the syringe-like nanorods, the LEE was enhanced by 10.5% and the radiation angle was shrunk from 136° to 121°. The results are attributed to the waveguide effect and the creation of graded refractive index profile at the interface between air and the device surface (Fig. 6). Po-Han Fu et al. also demonstrated the enhanced LEE by utilizing periodic SiO$_2$ nano-honeycomb arrays on the surface of LEDs, and achieved the output power enhancement of 77.8% [92]. Moreover, the output power is particularly enhanced at the diffraction angle around 65.1°, which is attributed to the intensive first order diffraction on the honeycombs. This result indicates that the emission pattern can be controlled by adjusting the dimension of nano-honeycomb [92].

4.2. Enhanced performance of GaN-based LEDs by substrate engineering

In addition to the TIR loss at the front side of LEDs, a large amount of downward-scattered photons are also lost or leaked into the substrate. Therefore, the LEE can be further improved once the downward-scattered photons can be restored. Moreover, the substrate also plays an important role in reducing lattice strain and defect densities in the device. Therefore, substrate engineering of GaN-based LEDs can contribute to IQE and LEE simultaneously.

4.2.1. Nanoscaled patterned substrates

Patterned sapphire substrates (PSS) have been widely used in commercial GaN-based LEDs due to the decreased TDs and increased light scattering. The nanoscaled PSS can provide higher pattern densities than micro-scaled PSS, leading to increased possibility of photon scattering and thus LEE [94]. Kao et al. reported the enhancement of LEE is achieved by increasing the aspect ratio of the nanoscaled PSS, which is attributed to the increased escaping probability of photons from the MQWs [95]. A novel method of PSS was reported by Cheng et al., who demonstrated the superior LEE attained via hybrid micro-nano PSS [96]. In spite of the enhanced LEE, many
studies demonstrated that PSS also provides the possibility to reduce the TDs in the epilayers. Y. Li et al., have utilized the nano-imprinting lithography to fabricate PSS, and used it for the growth of green GaN/InGaN MQW LEDs [97]. They found that screw dislocations and stacking faults in the active region are effectively annihilated. Based on these studies, the reduced TDs can be explained by three different observations: i) TDs initiated at the bottom of the etched

![Fig. 5. SEM images of the syringe-like ZnO NRs. The inset in (a) highlights the tapered ending on the top of the NRs. (b) Schematic of a typical syringe-like NR. (c) Microscope image of the ZnO NR before (left) and after (right) laser illumination. The 532-nm laser was injected into the NR at the bottom end (indicated by black arrow) and extracted out at the top end (white arrow) [91].](image)

![Fig. 6. Effective refractive index of a complex consisting of ZnO and air. (a) Schematics of the effective medium composed of ZnO and air, (b) the refractive indices of each layer in the GaN-based LED structure with ZnO nanorods, (c) the cross-sectional SEM image of the LED with ZnO NRAs, and (d) the effective refractive index profiles calculated based on the NRA light, which was measured from the cross-sectional SEM image [93].](image)
substrate are mostly stopped by the open voids; ii) TDs originating from the inclined facets change propagating direction, and therefore leave the MQWs; iii) only the TDs originating in the un-etched portions of the substrate propagate toward the active region. With PSS, it was found that TD densities can be lowered by 44% and IQE enhanced by a factor of 2.24 [97]. The transmission electron microscopy (TEM) image of the nanoscaled PSS as well as the enhanced IQE and EQE of the LEDs are presented in Fig. 7 [97].

### 4.2.2. Embedded nano-void substrate

For the LEDs with high LEE, high contrast of refractive index at the GaN/substrate interface is needed. To achieve the goal, many research groups carried out epitaxial lateral overgrowth (ELO) on patterned substrates to form air voids embedded in the epilayer close to the substrate [98–101]. The embedded voids can induce strong scattering considering the indices of GaN ($n = 2.4$) and air ($n = 1$), whose difference is much larger than that between GaN and sapphire ($n = 1.78$). The air void serves as an efficient scattering back-reflector in the device, promoting the chance of front-side emission. Moreover, the voids can also block or laterally bend TDs, hindering the formation of nonradiative recombination centers [3]. Chiu et al. grew the blue LEDs with embedded air voids and SiO$_2$ nanomasks and showed a 65% enhancement in light output power [102]. One should be noted that most of the reported methods for air voids are realized through the selective epitaxial lateral overgrowth (ELO) with SiO$_2$ passivation layer or metal nanoparticles to keep the voids during the overgrowth of GaN. Tsai et al. proposed an alternative way to generate embedded multi-layer nano-void photonic crystal LEDs [6]. They performed a nanosphere lithography and ELO, and obtained the air voids through the inherently different growth rates on the multiple facets of a nano-patterned substrate. A 151% enhanced light output power has been obtained by this method. In addition, IQE and efficiency droop behavior of the LED are significantly reduced due to the strain relaxation. Fig. 8 shows structure layout, TEM image, light output power and droop behavior of the LEDs with multi-layer nano-void arrays [103].
4.3. Nanorod and nanowire LEDs

The IQE, efficiency droop and switching speed of wurtzite InGaN/GaN MQW LEDs are seriously affected by the internal electrical fields related to spontaneous and piezoelectric polarization. To eliminate the strain-induced internal field, the most straightforward approach is to carry out the growth on semi-polar or non-polar substrates. Unfortunately, the cost of the semi-polar or non-polar substrates or hetero-epitaxial processes is too high for practical applications [104,105]. Nanorod or self-assembled LEDs are one of the promising approaches to mitigate the undesired lattice strain and the consequent piezoelectric polarizations. Compared with planar devices, engineering the geometry of LEDs provides more possibilities to address the issues of LEE, strain, and TDs, which are more or less related to the surface-to-volume ratio [106]. In this section, the recent progress of uniaxial nanorod and nanowire LEDs and three-dimensional (3D) core-shell nanorod MQW LEDs are reviewed.

4.3.1. Uniaxial nanorod LEDs

In general, the uniaxial nanorod (also called nanowires or nanocolumns) LEDs can be fabricated through top-down (etching the planar LED patterned by lithography) [107,108], bottom-up (nanorod growth) [109,110], or top-down followed by subsequence over-grown techniques [111]. Uniaxial nanorod LEDs have the advantages of strain relaxation, direct light out coupling and strong scattering [112]. Therefore, uniaxial nanorod LEDs are regarded as an alternative structure for high efficient GaN-based LED. Y.H. Ra et al. have grown vertically aligned III-Nitride nanowire LEDs on Si(111) by metal-organic chemical vapor deposition (MOCVD). High indium content (up to \( \sim 30\% \)) was realized in the uniaxial p-GaN/In\(_x\)Ga\(_{1-x}\)N MQWs/n-GaN nanorods owing to the superior strain relaxation [104]. A further investigation of strain distribution in the nanorod LED was reported by Wu et al. using a valence force field model [113]. The emission wavelength shift and spectrum broadening of nanorod LEDs were observed due to the strain relaxation at nanorod edge (15–20 nm), which means the better strain relief can be achieve by the nanorod with the smaller diameter (higher surface-volume ratio).
Carrier radiative life time in the MQW is also closely related to the relaxation of strain. According to the time-resolved photoluminescence studies, the fitted decay time at low temperature of 20 K is reduced from 25.34 ns (nanorod diameter = 300 nm) to 7.39 ns (nanorod diameter = 120 nm) [113]. As a result, the enhanced PL intensity can be observed in nanorod LEDs as compared to the planar LEDs due to the directly light out-coupling and strain relief characteristic of nanorod structure. With the superior strain relief characteristic of nanorods, Lin et al. reported phosphor-free full-color emission (white light) uniaxial nanorod on silicon substrate, as shown in Fig. 9. [114]. Sidewall passivation technique using organic sulfide especially octadecylthiol (ODT) has been found to mitigate Schockley-Read-Hall recombination and significantly enhance emission from the InGaN/GaN dish-in-nanowires grown on (100) silicon substrate using molecular beam epitaxy (MBE) technique [115]. In comparison with the un-passivated devices, the nanowire LEDs passivated by ODT not only exhibit higher peak efficiency, but also show a much faster increasing trend in quantum efficiency. Enhancement of optoelectronics performance of a passivated nanowire device has also been directed measured using a 4D electron microscope technique [116].

The four-dimensional ultrafast electron microscopy with time-resolved imaging capability was used to study the mechanisms of energy loss and carrier diffusion in InGaN/GaN disk-in-nanowires [117]. In the study, real-time visualization of the charge carrier dynamics on the surface has been observed. Most recently, red-wavelength InGaN/GaN disk-in-nanowire LED has been successfully grown on molybdenum substrate using MBE [118]. Broad emission wavelength from the nanowire LEDs have been consistently observed. From the study of monochromated low-loss electron energy-loss spectroscopy (low-loss EELS) on the InGaN nanodisks inserted in GaN nanowires, the emission wavelength broadening has been attributed to the large indium fluctuation in the nanowires [119]. The varied In-composition was found to cause a scatter in plasmon energies, resulting in the band-to-band transitions altered by the
The dielectric function of the nanowires ensemble. To further push the performances of nanowire LEDs, improving the uniformity of indium composition is an essential task. With increased indium compositions, highly efficient InGaN/GaN disk-in-nanowires laser emitting at 530 nm [120], 610 nm [121] and 1200 nm [122] have also been demonstrated.

Fig. 10. Core-shell nanowire LED grown on Si(111): (a) SEM micrograph of the as-grown p-GaN/InGaN MQW( × 5)/n-GaN core-shell, (b) array section covered with spin-on-glas and Ni/Au contacts, and (c) sketch of the nanowire array LED device. Electroluminescence (EL) measurements of a GaInN/GaN MQW nanowire array LED: (d) DC EL spectrum. The spectral window indicated by the shaded area was used for the time-resolved EL measurements, (e) high-speed measurement setup, and (f) time-resolved electroluminescence signal recorded at $V_{\text{DC}}=8$ V and $V_{\text{Pulse}}=6$ V square pulses for a pulse width of 500 ps and a frequency of 1.1 GHz and (g) a pulse width of 200 ps at a frequency of 1.3 GHz. The red points indicate the 90–10% rise- and fall-times. [46].

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4.3.2. Core-shell nanorod LEDs

To overcome the issues of polarization-induced electric field, growing LEDs on non-polar and semi-polar (m-plane and the a-plane), GaN substrates has been developed and is regarded as an effective way. However, this method is expensive and not yet commercialized at current stage. Alternatively, growing MQWs on the side walls of GaN nanorods (forming the core-shell structure) has been proposed as a cost effective approach to realize non-polar III-nitride LEDs. Moreover, high incorporation of indium is certainly necessitous for long wavelength LEDs, and this is another attractive feature of core-shell nanorod LEDs considering its reduced strain and very high surface-to-volume ratio. Li et al. found that the strain of InGaN thin film grow on GaN nanorods is two orders smaller than that of epitaxial InGaN thin film grow on the planar surface [123]. By this way, high indium (>40%) composition can be obtained with much higher lattice mismatch and strain related issues. The non-polar characteristic of core-shell nanorod LEDs are also expected to benefit high-speed visible light communication. In Fig. 10, Koester et al. grew core—shell GaN/InGaN nanorod LEDs on n-type Si(111) substrates, and reported a short radiative lifetime of ~110 ps at T= 7 K, which is attributed to the alleviated of spontaneous and piezoelectric polarization in the MQWs [46]. Time-resolved electroluminescence studies exhibit 90–10% rise- and fall-times of about 220 ps under GHz electrical excitation at room temperature. These results indicate core-shell nanorod LEDs can be used for high speed optical data communication.

For the photon extraction, as comparing with the conventional planar LEDs, the core-shell nanorod LEDs show advantages with their unique features of three-dimensional MQWs: the area
of MQWs is increased by a factor of $2h/r$ ($h$ and $r$ are the height and the diameter of a column, respectively) which can increase the photon generation at the same chip area. Moreover, the improved LEE can also be achieved based on light guiding and polarization characteristic of nanorod structure.

To compare the performances of the uniaxial and the core-shell nanorod LEDs, Y.H. Ra., et al., grew LEDs with two different structures as shown in the TEM images displayed in Fig. 11 (a) and (b) [104]. The consistently-aligned and uniform In$_x$Ga$_{1-x}$N/GaN ($x=0.08-0.38$) core-shell layers were grown coaxially on the $\{10\overline{1}0\}$ sidewalls of hexagonal c-axis n-GaN NWs on Si(111) substrates by MOCVD. Fig. 11(c)–(f) shows the electrical properties of the LEDs, where one can see the overall electrical properties and light output of the core-shell nanorod LEDs are apparently superior to that of uniaxial LEDs. The results were attributed to the absence of piezoelectric polarization in the core-shell MQWs. Also the wavelength shift with increased injection currents can be reduced with the (nonpolar) MQWs grown on the side walls.

### 4.4. Surface-plasmon-enhanced LEDs

Since the demonstration of a 14-fold enhanced photoluminescence intensity with the Ag-coated InGaN quantum well (QW) by Okamoto et al. in 2004 [69], surface plasmon (SP) enhanced LEDs have drawn intensive research efforts thereafter. The dramatic boost of light output was explained by the efficient coupling between the active region and the metal-semiconductor interface. In general, when the electron-hole recombination takes place in the QW, the released energy is transferred either to the radiative photons or to the nonradiative phonons. If the QW is in the near-field of the metal-semiconductor interface, a third channel of energy transfer can be included, namely the QW-SP coupling. The rate of QW-SP coupling is closely related to the frequency match between the emitted light and the electron oscillation in metal. In other words, if the metal electrons resonate with the frequency of the light generated from the QW, a very efficient QW-SP coupling can be achieved. The QWs with efficient QW-SP coupling have been shown with significantly increased spontaneous emission rates [69].

![Fig. 12](image)

**Fig. 12.** LED structures with metal nanoparticles employed to induce SP effect. (a) The nanoparticles embedded in n-GaN. (b) The nanoparticles inserted in the partially etched p-GaN.
For blue LEDs, silver (Ag) is the mostly used metal to attained SP effect, as the plasmon energy at the Ag/GaN interface is around 3 eV (410 nm) [69]. The plasmon energy of metal can also be tuned with specific geometric features and/or periodic arrangement [70]. It should be noted that, in order to maintain efficient QW-SP coupling, the QW has be no more than 100 nm from the metal interface. The constraint is due to the exponential decay of SP evanescent waves, and this imposes great difficulty in applying the SP effect to commercial LEDs, which usually require the p-GaN surface layer with the thickness greater than 150 nm to ensure low sheet resistance of the device. Therefore SP-enhanced LEDs are often demonstrated with the epilayers embedded with metal nanoparticles or the partially etched p-GaN in which nanoparticles are placed, as depicted in Fig. 12.

5. Enhanced performance of GaN-based solar cells via nanoscaled phenomena

Structuring semiconductor in nanoscale has been demonstrated as an effective route to achieve excellent AR properties, e.g. broadband working rage, omnidirectionality, polarization insensitivity, etc [124–127]. Fig. 13 displays various nanostructures fabricated on III-nitride solar cells. The different geometric features are generally obtained with either growth (bottom-up) or etching (top-down) processes. Moreover, surface plasmon effect has also been employed to improve the photovoltaic performances. Devices covered with these nanostructured surfaces are shown with much enhanced optical absorption in the active region, leading to improved EQEs and conversion efficiencies [128–130]. In addition to stronger optical absorption, the nanostructured solar cells also exhibit manifested strain relief and defect-density reduction, which significantly enhance the IQEs. In this section, the recent results of nanostructured GaN-based solar cells are reviewed.
5.1. Surface roughening

The high refractive index of GaN \((n \approx 2.5)\) prevents a significant portion of sunlight from propagating across the air/device interface \([131]\). Although the severe surface reflection is mitigated after coating with the transparent conducting oxide \((e.g.\ ITO)\) and the passivation layer \((e.g.\ SiO_2)\), the AR performances of these layered structures are usually not satisfactory in view of the broad solar spectrum. Roughening the GaN window layer surface via specific growth or process conditions is one of the most effective and industrially applicable methods to reduce the undesired interface reflection. InGaN-based light emitting diodes with optimized surface texturing has been reported to show dramatically enhanced light extraction efficiencies \([132]\). Similar approaches can be applied to nitride photovoltaic devices.

Surface morphologies of GaN epitaxial surface are generally controlled through growth temperature and V/III ratios. For instance, R.M. Farrell et al. texturized the p-type GaN layer with reduced substrate temperature and increased growth rates, attaining V-shaped pits on the surface \([57,133]\). It is found that EQEs of the InGaN solar cell can be increased by up to 27.1\% with the pitted surface \([133]\). Similarly, the GaN surface with dome-like microstructures is also achievable with properly controlled substrate temperatures and trimethylgallium flow rates, as demonstrated by Ho et al. \([134]\). Since the dimensions of the GaN microdomes are comparable to visible wavelengths, the microdome surface leads to greatly varied incident angles of the sunlight, being beneficial for light harvesting because of the strong scattering at the air/device interface. Compared to the device with flat surfaces, the InGaN/GaN multi-quantum-well solar cell with microdome surfaces brought about 102\% improvement of conversion efficiency \([134]\).

It is worthwhile to mention that the enhanced photovoltaic performances can also be attained by roughening the substrate surface. Lee et al. reported the 60\%-boosted photocurrents of InGaN-based quantum well solar cells by growing the structure on patterned sapphire substrates \([135]\). The substrate patterning was carried out by the wet etching in a mixture of sulfuric and phosphoric acids, which produces the surface displaying a trapezoid feature with \(\{1-102\}\) R-plane facets. Epilayers grown on the patterned substrate were found to exhibit reduced defect densities, resulting from the bending or annihilation of threading dislocations. The reduced defects lead to decreased capturing of photocarriers by the nonradiative recombination centers. In addition, patterning the substrate also results in strong optical scattering at the device/substrate interface, which contributes to the photocurrents through the increased photon recycling.

5.2. Rod-like nanostructures

Among the reported results, AR nanostructures are mostly formed with rod-like features, as the geometry can be relatively easily obtained with either top-down (lithography/etching) or bottom-up (growth) techniques. The nanorod structure can be directly fabricated with the p-type GaN window layer by dry etching using metal nanoparticles as the mask, which is naturally formed \(via\) thermal annealing of a thin metal \((e.g.\ Ni,\ Ag,\ Au,\ etc.)\) layer \([136]\). Alternatively, the rod-like nanostructure is also achievable on top of the GaN layer. For instance, SiO_2 nanorods can be fabricated with the process involving Ag-nanoparticle-based natural lithography and dry etching \([137]\). ZnO nanorods grown \(via\) the hydrothermal method also proved to be an effective approach for AR coating on InGaN solar cells \([138,139]\).

On a typical GaN-based solar cell, the surface is usually protected with a passivation layer, which can be SiO_2 or Si_{x}N_{y}. The passivation layer with properly selected thickness can reduce surface reflection at certain incident wavelengths. Nevertheless, as the absorption spectrum of the
InGa1-xN active region can easily span the wavelength range over 100 nm, the AR property displayed by a simple passivation layer is often less than satisfactory. For a nanostructured surface, the reflection is not only significantly lower than that seen with a quarter-wavelength layer, the extremely low reflection can also be sustained over a broad wavelength range. The superior AR performances of nanorods mainly comes from the disappearance of the abrupt air/device interface, where mismatch in refractive index between the two media can be large and thus results in severe optical reflection. Since the dimensions of the nanorods are generally below visible wavelengths, the incident solar light is not able to resolve the geometrical feature of the nanostructure, but sees it as an effective medium with the intermediate refractive index in the transition from air to the device. In other words, applying a nanorod structure on the InGaN solar cell replaces the discontinued refractive index at the air/device interface with a graded one, reducing the reflection through destructive interferences among the waves reflected from different depths in the nanorods [14]. The undesired reflection can be further suppressed if the

Fig. 14. (a) The scanning electron image showing SiO2 nanorod arrays (NRAs) hierarchically fabricated on the roughened p-type GaN (p-GaN) of an InGaN-based multi-quantum-well solar cell. (b) The EQEs of the multi-quantum-well solar cells with different surfaces, showing the superior performances brought by the hierarchical structure [137].
grading in refractive index is increased. The goal can be realized by shaping the nanorods into a syringe-like feature [138], or by hierarchically constructing the nanorods on top of the roughened (dome-like) p-type GaN, as shown in Fig. 14(a). Solar cells with the hierarchical AR surface are reported to reach considerably enhanced EQEs (Fig. 14(b)) [65].

5.3. Hole-like nanostructures

In addition to rod-like nanostructures, excellent AR performances are also attainable with the surface resembling a hole-like geometry. More importantly, the hole-like nanostructure is of superior optical and mechanical properties in comparison with its rod-like counterpart. Theoretical and experimental studies have shown that nanohole arrays can support higher density of waveguide modes than that within the nanorod arrays fabricated with the same filling factor [130,140]. Nanoholes also render stronger optical coupling with the incident sunlight [140]. These exceptional optical properties are particularly desirable considering the fact that improved AR capabilities are often obtained with lengthened nanorods, but the nanorods become increasingly fragile as their lengths exceed a certain limit. The superior light trapping capabilities of nanohole arrays allow them to reach sufficient AR performances with thinner thickness, which not only saves material cost but also improves mechanical robustness of the nanostructured AR layer [141].

Nanohole structures on GaN-based solar cells have been realized by several groups [142]. For instance, SiO₂ nano-honeycombs are applied on the p-type GaN window layer to trap the incident photons [142]. The nano-honeycombs are fabricated by dry etching of a thin SiO₂ layer, on which a monolayer of self-assembled nanospheres is employed as the mask. Alternatively, nanohole arrays can also be built with the p-type GaN [63], where similar nanosphere lithography is performed on device surface and Cl₂-based plasma is used to etch the GaN layer. Device characterization results reveal that the InGaN solar cells with the hole-like nanostructures exhibit the photovoltaic performances outrunning those with smooth or rod-like surface texturing [63]. As describe previously, the enhanced optical absorption is ascribed to the smoothed index transition at the air/device interface. The results of numerical analyses also indicate that the intensive light scattering induced in the nanoholes effectively broaden the field distribution within the device, benefiting the optical absorption by the InGaN active region [142].

5.4. Surface plasmon effects

Surface plasmon induces a resonantly enhanced near-field amplitude through the coupling of an external electromagnetic field to the charge oscillation in a metallic surface. If the amplified electromagnetic field is in the vicinity of the active region of a solar cell, improved optical absorption and thus the overall conversion efficiency can be achieved. The enhanced absorption is particularly important for InGaN-based active regions in light of the limited critical thickness of InₓGa₁₋ₓN grown on GaN, which often leads to the trade-off between solar absorption and crystal qualities [143,144].

In the structure design of InGaN-based plasmonic solar cells, one of the most important factors would be the emitter layer thickness. The thickness, i.e. the distance between the metal surface and the active region, determines whether the enhanced light intensities due to plasmonic effect can reach the absorbing layer. The selection of metal is another critical issue as it governs the wavelength of which the intensity to be amplified. Since the EQEs of an InGaN absorbing layer generally peak in the wavelength region of 370–450 nm [58,62,145], silver is considered as the suitable material for surface plasmon coupling on the GaN emitter surface (the plasmon
wavelength of Ag/GaN is around 410 nm) [146]. Numerical studies indicate that the performances of InGaN-based solar cells can be significantly enhanced by embedding Ag nanoparticles in the InGaN absorbing layer [147]. However, it is rather difficult to realize such device structure considering the high growth temperature of III-nitrides and the low melting point of Ag [148]. Pryce et al. employed an anodic aluminum oxide masking technique to apply Ag nanoparticles on the 200-nm GaN emitter of an InGaN quantum-well solar cell, and observed a 54% enhancement of EQE in UV wavelengths [149]. Although the enhancement of overall conversion efficiency under solar illumination (AM 1.5 G) is less significant because of the limited absorption in the visible region, the results demonstrate that Ag nanoparticles serve as plausible plasmonic scatterers for efficiency-enhanced InGaN solar cells.

5.5. Nanoarray solar cells

There are two kinds of junction structure for nanoarray solar cells: coaxial and planar junctions, as shown in Fig. 15. In comparison with the conventional light absorbing layer, where planar p-n junction is formed to separate photo-generated electron-hole pairs, the vertical active region made of aligned nanorod- (or nanowire-) arrays are of several advantages: i) As mentioned previously, the nanoarrays exhibit excellent AR properties, benefiting light absorption efficiency of the solar cell; ii) Surface area of the one-dimensional nanostructured p-n junction is much larger than that of planar devices, allowing more incident photons to reach the active region; iii) Defect densities in the heteroepitaxial nanorods can be much reduced because of the extended critical thickness on the foreign substrate, which results from the ultra-small contact area at the nanorod/substrate interface [150]. Reduced defect densities lead to elongated diffusion lengths of minority carriers, and thereby increase carrier collection efficiency of the device [151].

Coaxial n-GaN/i-In_{x}Ga_{1-x}N/p-GaN nanowires were first experimentally demonstrated using nanocluster-catalyzed MOCVD [152] and a similar core–shell vertical p-n junction consisting of n-GaN/InGaN-quantum-well/p-InGaN was demonstrated [64]. The coaxial p-n junction possesses a unique merit in addition to the three aforementioned advantages: a freedom to independently optimize solar absorption and carrier collection [152,153]. In coaxial p-n junction, decoupled directions of photon absorption and carrier collection in principle can greatly enhance photovoltaic performances of the devices. For a planar cell, one often faces the trade-off between absorption and carrier collection when determining the thickness of the absorbing layer. The dilemma can be circumvented in the core-shell nanostructure, where the p-n junctions are distributed along the sidewalls of the nanorods. In other words, optical absorption can take place

![Fig. 15. Schematics of the nanowire solar cells: (a) coaxial and (b) planar junction.](image-url)
deep into the nanoarrays and the photocarriers can be immediately collected by the junction field buried under the sidewall surface. In principle, such decoupled control over absorption and collection can significantly improve the photovoltaic performances of nanoarray cells. Moreover, the hetero-junction (p-type GaN nanorod arrays on n-type Si substrates) absorbing the light in UV and visible ranges with the band discontinuity at the GaN/Si interface preventing the undesired recombination of minority carriers achieved the efficiency of 2.73% under one-sun AM 1.5 G illumination [154], outperforming most of sapphire-based InGaN photovoltaic devices [63,64,138,150–153].

6. Conclusions and outlook

High refractive index difference, high threading dislocation density and strain-induced polarization field due to the nature characteristic of GaN-based material are the long-pending issues to obstruct the development of both GaN-based LEDs and solar cells. Unlike improving the efficiency via material growth or device structure design should satisfy the demand of LEDs or solar cells, respectively, a certain photon management technology base on nanoscaled phenomena can be utilized for both devices. For the mass production point of view, the nano-structure fabrication should be simplified to enhance IQE and photon extraction/harvesting simultaneously to reduce the cost. Based on the previous studies, 3D core-shell and uniaxial nanorod structure can satisfy this requirement to achieve high light extraction/harvesting, strain-free and high indium incorporation MQWs for highly efficient GaN-based LEDs and solar cells. However, the uniaxial nanorod devices are not suitable to use in high power or high brightness applications, due to the small area of active layer. In our best knowledge, the core-shell structure should be the promising approach to break the long-pending issues of GaN-based devices. It is worth pointing out that the 3-D modeling or measurement of carrier dynamics and photon extraction/absorption are very important for optimizing the structure (active layer structure, geometry of nano-structure, electrode and so forth) of core-shell devices and needs more exploration. Also, an effective surface treatment or passivation technology is needed for high surface-volume ratio nanostructured devices to reduce the surface recombination. We believe that with the progress in nanotechnology, cost-effective fabrication will be available, and the GaN-based devices based on nanotechnology would be an important candidate for next-generation photonic applications.

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