Evidence of carrier localization in AlGaN/GaN based ultraviolet multiple quantum wells with opposite polarity domains provided by nanoscale imaging

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Abstract

AlGaN based multiple-quantum-wells (MQWs) incorporating opposite polarity domains was grown by MOCVD. A direct demonstration of carrier localization effect was provided by a combination analysis of space-resolved luminescence peak position and Ga/Al composition distribution. Furthermore, through Raman spectroscopy, it is found that compressive strain plays a key role in improving the optical properties of UV-MQWs despite of the inferior crystalline quality in the N-polar domains. This suggests that incorporating sub-micrometer scale polarity domains in the MQWs is a promising perspective for the development of efficient UV emitters.

Keywords: Ultraviolet emitters, polarity control, carrier localization, nanoscale imaging

1. Introduction

Ultraviolet light-emitting-diodes (UV-LEDs) have drawn tremendous attentions in the past decade due to their wide applications in resin curing, water/air purification and biochemical sensing.1-6 However, the external quantum efficiencies (EQEs) of UV-LEDs are generally far lower than those of the InGaN based visible LEDs7,8 due to high-density defects, difficulties in p-type doping and larger polarization field in AlGaN thin film. This requires an in-depth exploration on the
optimized design of the active region in the UV-LEDs and deeper understanding on the carrier recombination processes.

Because of the non-centrosymmetric crystallographic orientation of III-nitrides, III- and N-polarity surfaces can be achieved along c-axis. Conventionally, III-polarity is more commonly used in device fabrication due to smooth surface morphology and high crystalline quality.\cite{9} N-polar surface, on the other hand, has many other advantages like increased carrier injection efficiency\cite{10} and reduced quantum-confined stark effect (QCSE) under forward bias condition.\cite{11} But, progress in growing N-polar epitaxial thin films is still lagging behind due to high densities of threading dislocations (TDs) and point defects, which strongly deteriorates device performance.\cite{12} This necessitates the search for novel optoelectronic devices taking advantages of both III- and N-polar domains.

It has been previously reported by Mita and Hite et al. that the polarities of III-nitride epitaxial thin films can be controlled by low temperature (LT) AlN nucleation layers (NLs).\cite{13} A macro-scale lateral polarity structure (LPS) was fabricated by substrate patterning followed by epitaxial growth through metalorganic chemical vapor deposition (MOCVD) with III- and N-polarity domains simultaneously grown side-by-side.\cite{14} Utilizing this structure, Collazo et al. reported a depletion-mode metal semiconductor field effect transistor (MESFET) on LPS-GaN with improvement in contact resistance.\cite{15} Sheikhi et al. reported the usage of LPS-GaN in the fabrication of Schottky barrier diode (SBD) with smaller on-state resistance and larger rectification ratio.\cite{16} Optical property of the LPS, on the other hand, has seldom been investigated in the past decades. Kirste fabricated an LPS-based GaN thin film, and observed a strong photoluminescence (PL) intensity at the domain boundary.\cite{17} It is noted that, once LPS is introduced into heterostructures like UV-LEDs, various interfaces will inevitably add to the complexity of the carrier distributions and recombination processes. A few works have been carried out so far.\cite{14,16-18} A recent study of our group demonstrated that by scaling down the size of both III- and N-polar domains to only several micrometers, and incorporating LPS into AlGaN/GaN MQWs, dramatically different optical behaviors were identified.\cite{19} Higher luminescence intensity was observed in N-polar than in III-polar domains, which can be ascribed to thickness fluctuations in N-polar domains as previously demonstrated by TEM.\cite{20,21} However, it must be noted that in addition to that, composition fluctuation and strain variation also play critical roles in the carrier localization effect, which has never been investigated before, and thus requires in-depth investigations, especially from the perspective of nanoscale mapping.

In this work, a direct demonstration of carrier localization effect is provided by a combined analysis of spatially resolved photoluminescence mapping, composition distribution and Raman
spectroscopy. The contribution from each factor is thoroughly discussed and the overall influence on the carrier localization effect is revealed.

2. Experimental Section

The epitaxial growth of UV-MQWs starts with the patterning of low temperature AlN-NL. Figure 1(a) schematically illustrates the fabrication process of an LPS with AlGaN/GaN MQWs and corresponding thickness/composition information. A 20 nm thick AlN-NL was firstly grown on a 2-inch sapphire substrate. The NL patterning was achieved using nanosphere lithography technique through polystyrene (PS) sphere coating followed by reactive ion etching (RIE). Self-assembled PS spheres on top of the AlN-NL were formed via a large-area micro-propulsive injection (MPI) method. Details on the preparation techniques were described elsewhere. The PS sphere diameters were then reduced by O₂ plasma trimming. The exposed LT-NLs in the gaps between PS spheres were etched by plasma etching using a mixture of Cl₂ and BCl₃ plasma with flow rates of 10 and 25 sccm, respectively, while the AlN-NLs beneath PS spheres remained intact. The bias and ICP powers are 100 and 300W during the process. The periodicity of AlN-NL patterning is 6 μm, with spacing between each pattern being 1.5 μm after etching. Patterned substrates were then re-loaded into the MOCVD chamber for epitaxial re-growth. Trimethylaluminum (TMA), triethylgallium (TEG) and ammonia (NH₃) were used as precursors of Al, Ga and N, respectively. The whole epitaxial structure of the MQW consists of 1 μm AlN thin film, 400 nm thick AlₓGa₁₋ₓN template with composition grading from x=0.6 to x=0.3, 600 nm thick Al₀.₂Ga₀.₈N template, and ten pairs of Al₀.₁Ga₀.₉N/GaN MQWs. 1 μm AlN template and epitaxial layers on top were grown at temperatures of 1250°C and 1100°C, respectively. For comparison purpose, uniform III- and N-polar MQWs were grown on uniform AlN-NL and bare sapphire substrates, respectively under the same growth condition.

Surface morphologies of the samples were characterized by Hitachi S-4800 field-emission SEM, and Veeco Dimension 3100V Atomic Force Microscope. Polarity identification was performed using the same AFM tool mentioned above, but operated under a scanned-probe mode based on the converse piezoelectric effect, i.e. piezoresponse force microscopy (PFM). Steady state PL characterization and time-resolved PL (TRPL) experiments were performed with a mode-locked Ti:sapphire laser at 5K. A third harmonic generator (APE-SHG/THG) was used to excite the samples by an output wavelength of 266 nm (pulse width 150 fs, pulse repetition rate of 76 MHz). Spatially resolved PL mapping was performed using a Renishaw inVia Reflex spectrometer system equipped with a 325 nm laser. Thin film composition and crystalline quality were characterized using Bruker D8 DISCOVER high-resolution X-ray diffraction (HRXRD). Relative atomic compositions were
studied by the nanoscale secondary ion mass spectroscopy (Nano-SIMS) using a Cameca NanoSIMS 50L system. Strain analysis and local thin film quality were carried out using the same equipment as that of PL mapping, but with a 532 nm Nd-YAG laser as excitation sources.

3. Results and discussions

Figures 1(b) shows the tilted view SEM images of the LPS sample. Circular-shaped III-polar domains and surrounding N-polar domains exhibit dramatically different surface morphologies due to variations in surface energies and consequently different growth modes.[25] The III-polar domains are slightly taller than adjacent N-polar domains. Several pit-like features within smooth III-polar domains are marked by black arrows, which could possibly due to either the existence of nanoscale inversion domains (IDs) or simply the formation of V-defect due to lattice and thermal mismatch.

The polarities of III-nitrides were identified by PFM as shown in Figure 1(c). Since III and N-polar domains have opposite spontaneous polarization fields, therefore PFM images are able to reveal different polarity domains through phase signal.[24] In-phase matching between the applied tip bias and the measured deflection signal is typically observed in N-polar domains, whereas the bias and deflection signals are out-of-phase for III-polar domains.[24] As clearly observed in Figure 1(c), III-polar domains are represented by out-of-phase signals with negative values, whereas N-polar domains are evidenced by the positive in-phase values. The colors near the interface between the III- and N-polar domains are relatively brighter, indicating a higher polarization field and stronger carrier accumulations there, consistent with previous reports from Kirste et al.[17]
Figure 1. (a) Schematic illustration on the fabrication process of lateral-polarity structures and corresponding structural information; (b) 30° tilted view SEM images of the as-grown LPS MQWs. Smooth III-polar domains and rough N-polar domains are notified. Pit-like features inside III-polar domains are indicated by black arrows; (c) Corresponding PFM phase signals of the LPS for polarity identification.

To understand the optical behaviors of the MQWs with opposite polarity domains, steady-state PL spectra were firstly collected on uniform III-polar, N-polar and LPS MQWs respectively at 5K. Pumping power was kept as 50 mW/cm². As shown in Figure 2(a), LPS sample exhibits the strongest PL intensity, demonstrating its high radiative recombination efficiency compared to uniform polar samples. Furthermore, the luminescence intensity of uniform N-polar sample is higher than that of the III-polar sample. This could be originated from the rough surface morphology, and consequently strong carrier localization effect induced by the composition and thickness non-uniformity in N-polar sample. The strong PL intensity in the N-polar surface is consistent with the CL mapping shown in our previous work, where quantum-dot-like luminescence centers were observed.\cite{20} Peak positions for uniform III-polar, N-polar and LPS MQWs are 355 nm, 360 nm and 350 nm, respectively. More than 10 nm peak shift is observed among all samples. Since all the samples were grown in MOCVD chamber at the same time, the discrepancy of peak emission wavelengths can be ascribed to different carrier confinement properties within different polarity domains of the MQW region.\cite{25} Inside the LPS-based MQW, the distribution of PL peak position was further analyzed by spatially-resolved PL...
mapping. The 3D mapping of peak position in a 20×20 \( \mu \text{m}^2 \) region is shown in Figure 2(b). Interestingly, a negligible 4 nm peak variation was obtained between III- and N-polar domains within the LPS sample, and there is no correlation between the peak maximum or minimum and the locations of the polarity domains. This strongly suggests that the 10 nm blue shift in the LPS from Figure 2(a) is not solely dependent on thin film polarity.

![Figure 2](image)

**Figure 2.** (a) PL spectra of uniform III-polar, N-polar and LPS MQWs collected at 5K; (b) 3D color map of the emission wavelength distribution within LPS MQW sample

Note from Figure 2(a) that uniform III-polar MQW exhibits the lowest PL intensity. In order to investigate the influence of crystalline quality on the optical behaviors, XRD rocking curves (RCs) on (002) diffraction peaks of MQW region were characterized and shown in Figure 3(a). The full-width-half-maximum (FWHM) of the diffraction peaks are 0.334°, 0.435° and 0.317° for uniform III-polar, uniform N-polar and LPS samples, respectively. The threading dislocation densities are calculated to be 3.1 \( \times \) 10^9 cm\(^{-2} \), 5.3 \( \times \) 10^9 cm\(^{-2} \), and 2.8 \( \times \) 10^9 cm\(^{-2} \). Referring the low PL intensity of uniform III-polar sample, it is concluded that optical property has weak dependence on crystalline quality. In fact, the relatively higher PL intensity in N-polar and LPS samples can be explained by the composition and thickness non-uniformity in the MQWs. This leads to carrier localization effect and much stronger radiative recombination rate in the active region, which has been reported in our previous work.\([27]\) Figure 3(b) shows the \( \omega \)-2 \( \theta \) scans of all samples. The 0\( _{\text{th}} \) order peaks of MQWs are located at 2 \( \theta =34.59^\circ \), 34.60° and 34.65° for uniform III-polar, N-polar and LPS samples. Therefore, the average Al compositions in the MQW active regions are 1.6%, 2.3%, and 5.8%. Note that these are average values considering the composition and thickness of both Al\(_{0.1}\)Ga\(_{0.9}\)N QB and GaN QW. The variation is possibly due to different adatom incorporation rates in III- and N-polar surfaces and influence from rough surface morphology. Also notice that the XRD peak position of
Al$_0.2$Ga$_{0.8}$N template follows the same trend, suggesting that composition variation already started during the AlGaN template growth. Nevertheless, if the PL emission is solely dependent on Al composition, then a maximum 7.7 nm peak shift is obtained (361.8 nm, 360.5 nm and 354.1 nm for above three samples derived from the average MQW composition). This result is obviously against the large variation of PL wavelengths as shown in Figure 2(a). Therefore, the investigation of optical behaviors of these samples should consider not only thin film composition, but also carrier localization effect as mentioned before.

**Figure 3.** Symmetric (002) XRD rocking curve scans of the MQWs from uniform III-polar, N-polar and LPS samples (a); $\omega$-2$\theta$ scans of these three samples for composition analysis

To further understand the carrier dynamic properties of the UV-MQW samples, time-resolved and wavelength dependent TRPL study of uniform III-polar, N-polar and the LPS samples are compared in Figure 4(a). The $x$ axis denotes the wavelength, and the $y$ axis is the relative time. The decay profiles of all the samples depend on the wavelength. For uniform III-polar sample, two dominant emission peaks are observed at 340 and 350 nm, respectively. The 350 nm peak shows a much stronger intensity and also relatively slower decay curve. For uniform N-polar sample, three peaks can be identified, locating at 352, 355 and 358 nm, respectively. These three peaks might be
correlated with different energy states in the MQWs due to thickness fluctuations in the N-polar MQW region.\cite{20} In comparison to uniform III- and N-polar MQWs, LPS-MQW shows a rather uniform decay profile. Only one single peak at 347 nm was identified. At peak wavelengths, time-resolved PL intensity of LPS MQW and uniform polar MQWs all follow a mono-exponential decay as shown in Figure 4(b), suggesting the negligible influence from non-radiative recombination at low temperature. After calculation, the decay lifetimes of uniform III-polar, N-polar MQWs and LPS MQW are 1.79, 1.96 and 0.56 ns, respectively. The shortest decay lifetime of LPS-MQW suggests a much faster recombination channel and consequently higher radiative recombination rate.\cite{28, 29}

![Figure 4](image)

Figure 4. Temporal and wavelength dependent PL spectroscopic profiles at 5 K of uniform III-polar, N-polar and LPS-based MQWs (a), and mono-exponential decay curves at peak wavelengths for all three samples

As identified above, there is a wavelength variation among the PL spectra of uniform III-, N-polar and LPS-based MQWs. Control of the emission wavelength is challenging since it is related to various factors including alloy compositions, QW confinement, strain conditions of the active regions.\cite{30, 31} Introduction of different polarity domains into the system makes it even more complex. Thus, it is crucial to distinguish the contribution of each factor. Herein, nano-SIMS characterization of the LPS was performed with a collection depth near the surface where the MQWs are located. Figure 5(a) highlights the different element concentrations between III- and N-polar domains of the LPS samples with 6 µm periodicity. Line scans from two locations are taken to qualitatively analyze the Ga/Al ratio. As marked by the solid line, Line 1 scans across several domains while line 2 presents the relative Ga/Al composition within the N-polar domain, and the results are shown in Figure 5(b)
and (c), respectively. A higher Ga concentration is revealed in the N-polar than that of the III-polar domains, and the intensity difference reaches 38%. It is well known that Al has smaller diffusion length than Ga atoms,[32] thus the lateral transportation in AlGaN is mainly contributed by Ga. Additionally, the lateral diffusion of Ga atoms across the domain boundaries is not uniform due to different surface energies of III and N-polar domains. Therefore, the large composition difference in adjacent polarity domains is originated from the net mass transport of Ga atoms from III-polar to N-polar domains. This result is consistent with the height difference between two domains in bulk AlGaN LPS as previously reported by Hoffmann et al. [33] Within the N-polar domains, the distribution of Ga and Al is also not uniform. Quantum-dot like features are observed, which are probably caused by the local Ga-enrichment. The average intensity variation is 17%. It must be noted that the MQW consists of AlGaN QB and GaN QW. Therefore, higher Ga/Al ratio in N-polar domains revealed by nano-SIMS means either a higher Ga content in AlGaN QB or a relatively thicker GaN QW (or thinner AlGaN QB) in the N-polar domains. Both factors can contribute to carrier localization effect.[9] In fact, thickness fluctuations in N-polar domain were observed in our previous work, in which case QW/QB non-uniformity was identified in N-polar domain by cross-sectional TEM, while sharp interface and uniform QW/QB thickness were obtained in III-polar domain. [26] This would lead to potential minima in the band structures with strong carrier localization effect. As a result, luminescence intensity can be greatly enhanced.

![Figure 5](image_url)

**Figure 5.** (a) Nano-SIMS imaging of the Ga/Al ratios on the surface of the LPS. Red/yellow color represent larger Ga incorporation, whereas blue color represents smaller Ga
incorporation. (b) and (c) are the line scans 1# and 2# of the intensity ratios as marked in the color map

Considering that N-polar domains in the LPS have higher Ga content than adjacent III-polar domains if the MQW region is treated as a whole, one would assume that the luminescence peak position of the LPS MQW would be located between those of uniform III and N-polar samples since it is a combination of high-Ga-content N-polar domain and low-Ga-content III-polar domain. To the contrary, the PL position of LPS sample is the shortest compared to those of the uniform III and N-polar ones as shown previously in Figure 2 (a) and Figure 4 (a). Therefore, peak positions of the PL spectra are not exclusively influenced by the average MQW composition, but also by other factors such as strain conditions.\[^{34}\] In order to demonstrate that, Figure 6 (a) shows the large-scale Raman spectroscopy of the uniform III-polar, N-polar, and LPS samples. The modes of Al\(_2\)O\(_3\)-E\(_g\), Ga\(_N\)-E\(_2\) (high) and Al\(_N\)-E\(_2\) (high) are clearly observed in the spectra. Compared to uniform III-polar and N-polar samples, the position of the Ga\(_N\)-E\(_2\) (high) Raman peak shift right by approximately 4 cm\(^{-1}\). Note that larger Ga\(_N\)-E\(_2\) (high) Raman shifts are usually associated with increased compressive strains or increased Al composition in Al\(_{Ga}\)N.\[^{35, 36}\] The latter disputes earlier findings of lower Al content (i.e. higher Ga/Al ratio) in N-polar domains demonstrated by Nano-SIMSs. Therefore, stronger compressive strains in the N-polar than in III-polar domains must be responsible for the observed Raman peak variation.\[^{37, 38}\] A conclusion can be safely drawn that the blue shift in PL spectra of LPS is mainly correlated with the strong compressive strains inside the LPS structure. A spatially-resolved micro-Raman distribution of Ga\(_N\)-E\(_2\) (high) mode positions is shown in Figure 6(b). N-polar domains exhibit larger Ga\(_N\)-E\(_2\) (high) Raman shift compared to III-polar domains. Similarly, N-polar domain has stronger compressive strain than that of III-polar domain. The stronger compressive strains in the N-polar domains can be explained by either higher Ga content and thus larger lattice constant of N-polar thin film in average, or crystal coalescence due to the 3D growth nature of N-polar Al\(_{Ga}\)N thin films.

Finally, it needs to be pointed out that, the FWHM of the E\(_2\) (high) mode is an indicator for the crystalline quality of epitaxial thin film.\[^{17}\] As shown in Figure 6(c), FWHM values of Ga\(_N\)-E\(_2\) (high) mode in N-polar domains are larger than those in III-polar domains by approximately 5 nm. This can be explained by the existence of high density of grain boundaries and point defects since N-polar surface are easier to incorporate impurities such as oxygen.\[^{39}\] Interestingly, poor crystalline quality does not necessarily result in a poor optical behavior. Carrier localization and enhanced compressive strains compensate the disadvantage of crystalline quality, and contribute to the superior optical properties of the LPS-MQW.\[^{40}\]
Conclusions

In conclusion, AlGaN/GaN based ultraviolet MQWs with opposite polarity domains were successfully fabricated on a single sapphire substrate. III- and N-polar domains were confirmed by piezorespons force microscopy. Stronger photoluminescence intensity, shorter wavelength and higher radiative recombination rate were illustrated for LPS-MQW. The superior optical property of the LPS MQW was ascribed to carrier localization effect as demonstrated by a thoroughly investigations on spatially-resolved PL mapping, Ga/Al distribution, and strain distribution. This work provides a direct evidence of carrier localization effect by numerous nanoscale imaging techniques, and suggests that LPS-based MQW is beyond simple combination of III- and N-polar surfaces, offering novel perspective in the realization of high-efficiency UV-emitters.

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Conflict of Interest

The authors declare no conflict of interest
Evidence of carrier localization in AlGaN/GaN based ultraviolet multiple quantum wells with opposite polarity domains provided by nanoscale imaging

TOC image: (a) Large-scale Raman spectra of uniform III-polar, N-polar and LPS samples; Spatially-resolved map of the Raman shift positions (b) and FWHM distributions (c) of the GaN-E₂(high) mode of LPS. N-polar domain exhibits stronger compressive strain, contributing to the blue shift in PL spectrum
References


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