Deep ultraviolet (DUV) light-emitting devices have a variety of useful applications, including germicidal irradiation, phototherapy, water, air, and food sterilization, charge management in space-based sensors and photocatalysis, among others. Although Hg vapor-based lamps have traditionally served as UV light source for these applications, their effectiveness is severely limited due to bulkiness, slow response time, fragility, temperature sensitivity, high power consumption, and potential environmental hazards. As such, AlGaN-based light-emitting diodes (LEDs) are considered a viable alternative by both researchers and industry practitioners, as their use eliminates the aforementioned drawbacks, while offering the advantage of wide spectral tunability for a multitude of applications. While AlGaN-based DUV LEDs have been achieved in a research context, their industrial success has been limited, primarily due to poor external quantum efficiency (<15%). Recently, extensive work on AlGaN-based DUV LEDs has been conducted to enhance epitaxial growth quality and improve device internal quantum efficiency (IQE) by reducing the threading dislocation (TD) density arising from the lattice mismatch between the grown materials and substrates. Many growth enhancement techniques have proven successful in improving the IQE of AlGaN-based DUV LEDs. For instance, a thick AlN template on sapphire has been used to reduce TD density through the epilayers, thereby increasing the overall efficiency of the III-nitride-based devices. Strained-layer superlattices (SLSs) have also been employed to improve epitaxial morphology of the resulting devices. Previously, by combining SLS with a nanopatterned sapphire substrate, the IQE value of the DUV AlGaN/AlGaN multiple quantum well (MQW) has been enhanced. Although, the use of homoeptaxial (native AlN) substrates renders these structure-enhancing techniques redundant by ensuring that devices are free from TDs, such DUV devices still suffer from low external efficiency, accompanied by a droop at high carrier densities. However, other structural enhancements, such as spontaneous subwell formation, that can improve the device efficiency have not yet been studied. Particularly, no research on carrier dynamics has been conducted to investigate the effect of subwells/sub-barriers surrounding MQW structures.
on the DUV device efficiency and the contributions of the nonradiative and Auger recombination. In this work, we reveal the carrier dynamics of a DUV AlGaN/AlGaN MQW structure grown on native AlN substrate. The advanced structural investigations reveal the presence of subwell and sub-barrier layers sandwiching the MQWs in the active layer. Optical analyses show the effect of these understudied structural aberrations on the carrier dynamics, optical efficiency and efficiency droop inside the active regions.

## SAMPLE GROWTH AND EXPERIMENTAL TECHNIQUES

The DUV structure was prepared by metalorganic chemical vapor deposition (MOCVD). Trimethyl-aluminum (TMAI), trimethyl-gallium (TMGa), and NH₃ were used as the precursor reactants. A 400 nm thick AlN buffer layer was initially grown on a 1 in. thick (0001) AlN substrate at 1250 °C, followed by a 20 x Al₅Ga₄N/Al₅Ga₅N (3 nm/12 nm) multiple thick n-AlGaN layer was grown, followed by a nominal 1.1 μm plan-view STEM image of the AlGaN/AlGaN LED structure grown of AlN substrate; (b) 2.7 × 2.7 μm plan-view STEM image of the sample.

![Figure 1](https://dx.doi.org/10.1021/acsphotonics.9b01814)

**Figure 1.** (a) STEM cross-sectional image of the AlGaN/AlGaN MQW structure lamellae were prepared for high-angle annular dark field—scanning transmission electron microscopy images (HAADF-STEM) using an FEI Helios focused ion beam (FIB) and scanning electron microscope (SEM). The HAADF-STEM images were acquired using a Cs-probe corrected FEI Titan HR-STEM system, operated at an acceleration voltage of 300 kV. EDX maps were acquired using the system attached to FEI Titan HR-TEM. For photoluminescence (PL) measurements, the third harmonic line (250 nm) of an ultrastar (150 fs) Ti:sapphire pulsed laser (76 MHz) served as the excitation source. The emitted signal was subsequently spectrally resolved using a SpectraPro 2300 spectograph fitted with a grating with 150 gr/mm groove density and a blaze of 300 nm. A Hamamatsu C9300 charge-coupled device (CCD) camera detected the emission arising from the sample. The excitation source was focused to a beam diameter of ~60 μm for power-dependent PL measurements to enhance the power density incident on the sample. For temperature-dependent time integrated (TIPL) and time-resolved PL (TRPL) measurements, the sample was enclosed in a Janis ST-100 closed cycle cryostat under high vacuum conditions. A LakeShore 335 temperature controller was employed to vary the sample holder’s temperature within the 5–300 K range. To temporally resolve the detected signal, the excitation pulse frequency was first reduced to 2 MHz using A.P.E PulseSelect pulse picker, after which a Hamamatsu C5680 streak camera with a slow sweep unit, fitted between the CCD and the spectograph, was activated. Each sweep signal was synchronized with the reduced pulse frequency of the excitation source. The detected signal was subsequently acquired in photon counting mode. Room temperature (RT) PL excitation (PLE) was carried out using FLS1000 Edinburgh Instruments spectrometer attached to a 1000 W Xe lamp. APSYS, a commercial TCAD software developed by Crosslight Inc., was used to numerically simulate an LED device with a similar active region as the DUV structure. The software self-consistently calculates Poisson’s equation, the current continuity equation, the carrier transport equations and the quantum mechanical wave equations of the device, from which information, such as the current-dependent IQE, position dependence of the bandgap energy, carrier concentration in the active region, and carrier recombination rates can be extracted.

### RESULTS AND DISCUSSION

Figure 1a shows the cross-sectional STEM image of the full sample structure. The thicknesses of the various pre-MQW layers indicated in the STEM image are typical of similar structures grown on sapphire. As expected, no TD defects are observed, as confirmed in the HR-STEM plan-view images of the structure shown in Figure 1b, where no evidence of spots that are characteristic of TD defects is found. This is not surprising, considering that the MQWs are preceded by an AlN buffer layer that was homoepitaxially grown on an AlN substrate characterized by very low TD density (typically <10⁴ cm⁻²). In addition, the SLS structure further mitigates the propagation of TDs to subsequent layers.

A magnified image of the MQWs and EBL layers is shown in Figure 2a, further confirming that the MQWs are well-defined, with no apparent interruptions from TDs. Figure 2b shows a magnified STEM image of a single quantum well, indicating presence of ultrathin layers sandwiching the MQWs. To further identify these layers, EDX was carried out during HR-TEM measurements to study the chemical composition of Ga, Al, and N content, as shown in Figure 2c. The chemical composition profile shown in Figure 2d reveals that all MQWs are neighbored by a shallow subquantum well (sub-QW) on one side, which has a lower Ga concentration (indicated by a black arrow in Figure 2d) compared to that in the main MQWs, and is separated by an ultrathin barrier from the main MQW (<1 nm). On the other edge of the MQWs, an additional Al-rich layer forms, providing further ultrathin barrier (sub-QB) of <1 nm width and characterized by a slightly higher Al concentration compared to the quantum barrier (QB), as indicated by the red arrow in Figure 2d. This distribution was confirmed for all MQWs, as shown in Figure 2d. Such sub-QB structures have previously been observed and were attributed to a “compositional pulling” effect, where the smaller of the group-III atoms (Al) preferentially drift toward the barrier layer that exerts a compressive strain on the well during MOCVD growth.

Figure 3a shows the PL spectra of the structure at 5 and 290 K (RT), indicating that, at 5 K, the main MQW PL peak is
located at 4.57 eV and is slightly red-shifted to 4.55 eV at RT. However, a slight shoulder at 4.44 eV is visible on the lower energy side of the spectrum. The ratio of integrated intensity at RT and at low temperature, $A(290\,\text{K})/A(5\,\text{K})$, was found to be 81%, confirming high optical quality. The temperature-dependent ratios of the integrated intensity, $A(T)/A(5\,\text{K})$ (linked red circles), and peak intensity, $I(T)/I(5\,\text{K})$ (linked green circles), are plotted against temperature ($T$) in the inset of Figure 3a. Note that, as no TD propagation to MQWs was observed, $A(T)/A(5\,\text{K})$ is a qualitative representation of the IQE values of the MQW emission, based on the assumption that, at cryogenic temperatures, carriers lack the thermal energy required for their capture by nonradiative centers around TD defect sites, according to Rashba’s treatment.$^{33−36}$ At any rate, the occurrence of TD density is expected to be very low in Al-rich AlGaN epitaxial layers grown on AlN substrates (as the structure is grown on a lattice-matched substrate).$^{37,38}$ Thus, in such a structure, the increased distance between nonradiative centers reduces the probability of nonradiative recombination.$^{39}$ Therefore, high IQE values are expected of structures exhibiting high crystalline quality free from TDs. On the other hand, as the temperature increases, there is a notable divergence between the slopes of the integrated intensity ratio, $A(T)/A(5\,\text{K})$, and the peak intensity ratio, $I(T)/I(5\,\text{K})$. This temperature-dependent difference indicates that carrier redistribution (affected by the potential differences between the MQWs and sub-QWs) plays a significant role in the recombination dynamics of the structure.

To elucidate the carrier distribution phenomenon further, the PL centroid (defined as the weighted average peak of all the photon energies represented in the PL emission spectrum ranging, in this case, from 4.30 to 4.80 eV),$^{40}$ as well as the full width at half-maximum (fwhm) of the emission spectrum and peak energy, are plotted (in Figure 3b) as functions of temperature. At 5 K, the peak energy is located at $\sim$4.57 eV, whereas the peak abruptly redshifts to $\sim$4.55 eV in the 30−75 K temperature range, after which the peak energy remains unchanged as temperature increases to 290 K. Given that the
peak energy is virtually independent of temperature above 75 K, a direct relationship between bandgap shrinkage and temperature increase due to thermally induced dilation of the crystal lattice can be ruled out. Indeed, this independence can be attributed to strong carrier confinement within the MQWs, with the peak energy centered at \( \sim 4.55 \) eV. Such strong confinement in the MQWs is aided by the Al-rich sub-QB layers, which act as additional high-energy barriers in the structure. On the other hand, the initial redshift in peak energy as the temperature increases from 30 to 75 K is attributed to rapid thermionic repopulation of randomly distributed carriers from weakly confined states in the shallow sub-QWs at very low temperatures to the main recombination sites within the MQWs through tunneling and hopping, as the ultrathin QB between MQW and sub-QW is only \(<1\) nm thick.

The fwhm plot shown in Figure 3b reveals that the line width broadens as the temperature increases, starting from \(\sim 100\) meV at 5 K, and reaching a saturation value of \(\sim 140\) meV in the 190–290 K range, confirming our hypothesis. This broadening indicates that, after settling at the main MQW recombination sites, thermal delocalization causes a proportion of the carriers to migrate to other recombination centers in the vicinity of the localized recombination site at 4.55 eV. However, since the peak energy remains practically constant above 75 K (which is lower than the saturation temperature of the fwhm), the PL centroid energy plot as a function of temperature was studied to determine the carrier flow direction. The PL centroid energy plot should be sensitive to the energy state of the migrating carriers since it is a weighted average peak of all the photon energies represented in the PL spectrum. As shown in Figure 3b, in the 5–100 K range, the centroid energy decreases as the temperature increases. Here, saturation is achieved at 190 K, following an opposite trend to that shown in the fwhm plot. This observation suggests that, aided by thermal excitation, a small fraction of migrating carriers has red-shifted (4.535 eV) to energy states located below 4.55 eV.

To further understand the carrier dynamics of the MQW structure, it was subjected to temperature-dependent TRPL measurements, as indicated in Figure 4a. The lifetime values were obtained by fitting the experimental data (dots) to the biexponential lifetime decay model (lines; see Section S2 in Supporting Information for details) due to different recombination centers. Figure 4b shows the PL lifetime \(\tau_{PL}\) (black spheres) as a function of temperature. Interestingly, no obvious \(\tau_{PL}\) dependence on temperature is observed, confirming strong dominance of radiative recombination. It is known that the radiative recombination rate is independent of temperature.

In order to study the specific roles of radiative and nonradiative processes and the carrier dynamics within the MQWs, the radiative \(\tau_{Rad}\) and nonradiative \(\tau_{Non-rad}\) lifetimes of the carriers with respect to temperature were extracted from the PL lifetimes, as shown in Figure 4b.
No crossover point has been observed for the studied temperature range, as the radiative lifetime is dominant. The obtained findings revealed that $\tau_{\text{Non-rad}}$ declines monotonically from 1300 ns at 15 K to 40 ns at 290 K, as shown in Figure 4b. While this represents a significant reduction in the $\tau_{\text{Non-rad}}$ value within the temperature range of interest, it has negligible effect on the overall carrier lifetime of the MQWs ($\tau_{\text{PL}}$). On the other hand, $\tau_{\text{Rad}}$ of 7 ns was obtained at 5 K and remains constant until 90 K. This temperature range (5–90 K) coincides with the range at which an abrupt redshift in peak energy occurs, as shown in Figure 3b. Since the significant carrier migration to the localized recombination sites ($\sim$4.55 eV) observed in this range (5–90 K) has no notable influence on the radiative efficiency (IQE = $A(T)/A(5 \text{ K})$) of the MQWs, as indicated in the inset of Figure 3a, it is proposed that the constant $\tau_{\text{PL}}$ is due to a dynamic equilibrium between the rate of carriers (from shallow sites in the sub-QW) captured by the localized sites within the main MQW (at 4.55 eV) and carrier escape from the main sites to other lower energy states, as shown in Figure 4c. These lower-energy sites can be due to lateral inhomogeneities in the MQWs.21,22

At high temperatures ($T > 220 \text{ K}$), the carriers approach thermal equilibrium, due to which they become randomly distributed across the main MQW, sub-QW, and lower-energy sites, as shown in Figure 4e. Thus, the resulting emission will be due to transitions from all these sites. Notably, it is within this temperature range that the fwhm approaches its saturation value of 140 meV, indicating that, at this point, most of the states have reached thermal equilibrium and there is no net carrier migration, as illustrated in Figure 4e. Figure 5a shows that the RT PLE spectrum obtained at the MQW emission peak (4.55 eV) presented in Figure 3a, which indicates that such emission originates from two sources, the MQW band edge (located at 5.08 eV) and an additional higher-energy edge located at 5.48 eV. The higher-energy edge can be due to the transitions from the sub-QW. This result confirms our hypothesis that the carriers approach thermal equilibrium and are distributed across all sites. However, the contribution from the main MQW states predominates due to the higher density of states compared to the other two types (sub-QW and lower energy states).

We simulated an LED device with similar sub-QW, sub-QB, MQW and QB in its active region (see Section S3 in Supporting Information and Figure S3) to gain insight into the distribution of electrons and holes in the active regions, as well as to estimate the recombination efficiency of the active region (MQW, sub-QW, and sub-QB, as shown in Figure S4). The simulated LED was subjected to an injection current of 10000 A/m$^2$, while the nonradiative lifetime, radiative recombination coefficient and Auger recombination coefficients were set at 8 ns, $4 \times 10^{-7}$ cm$^3$/s and $3 \times 10^{-30}$ cm$^6$/s, respectively, consistent with commonly made assumptions.18,49,50 The band
yielding the signiﬁcant onset of Auger recombination. The inset of Figure 5c shows the position dependence of electron and hole concentrations in the active region. It is noteworthy that, while the simulation showed that most of the carriers are concentrated within the MQWs, as expected, it indicated that still a small fraction of carriers are inside the sub-QW layers, supporting the observation previously made by PLE. We carried out power-dependent PL spectroscopy at RT, which allowed us in order to systematically study the IQE values and efficiency droop of the MQW emission, as well as the effect of nonradiative recombination, using the Shockley–Read–Hall (SRH) method, where the excitation pulse power-dependent carrier generation rate, \( G(P) \), is given by

\[
G(P) = An(P) + Bn(P)^2 + Cn(P)^3
\]

(1)

where \( An(P) \) represents the Shockley–Read–Hall (SRH) nonradiative recombination rate, \( Bn(P)^2 \) is the radiative recombination rate, and \( Cn(P)^3 \) is the Auger nonradiative recombination rate. The integrated PL intensity can be deﬁned as \( I_{PL} = \beta Bn^2 \) (here, we have adopted \( A_{PL}(T) = I_{PL} \) to differentiate between \( A \) of the SRH coefﬁcient and the integrated intensity \( A(T) \), and \( \beta \) represents a constant determined by the total collection efﬁciency from the active region volume). Hence, eq 1 can be rewritten in terms of \( I_{PL} \) yielding

\[
G(P) = A \left( \frac{I_{PL}(P)}{\beta B} \right) + I_{PL}(P) \left( \frac{C}{\beta B} \right)^{1/2}
\]

(2)

This equation shows the three regimes as a relation between carrier generation rate \( G \) and PL intensity \( I_{PL} \), given by \( I_{PL} \propto G^k \), whereby \( k = 2 \), applies to a nonradiative SRH recombination regime at low carrier injection; \( k = 2/3 \) relates to the Auger recombination regime at high carrier injection; and \( k = 1 \) holds where a radiative recombination regime dominates.\(^5\)

According to the SRH method described by eq 1, the power-dependent IQE can be derived with the following equation, as explained elsewhere:\(^4\)

\[
\text{IQE}(P) = \frac{Bn(P)^2}{G(P)}
\]

(3)

The curve depicting IQE as a function of excitation pulse power density is presented in Figure 5d, where an increase in IQE with power density can be observed up to a maximum value of \( \sim 83\% \) at \( 15 \text{ MW cm}^{-2} \). This value is comparable with both the thermal IQE determined by the integrated PL intensity ratio, \( A(290 \text{ K})/A(5 \text{ K}) \) and the numerically simulated IQE result. This value is also in accordance with the IQE reported previously for AlGaN/AlGaN MQWs grown on native AlN substrate.\(^18\) However, beyond this point, a slight efﬁciency droop that sets at \( \sim 60\% \) was noted, indicating the signiﬁcant role of the exciton localization in the sub-QW states.

In general, four possible mechanisms have been proposed as the cause of efﬁciency droop in III-nitride quantum wells, namely, Auger recombination,\(^54,55\) carrier overﬂow/delocalization from the quantum well into the p-region, which is not an efﬁcient radiative recombination center,\(^6,57\) defect-assisted tunneling,\(^58,59\) and current density assisted defect recombination.\(^60\) However, we rule out the latter two mechanisms as the main cause of the droop in our MQW structure, given that it is practically TD-free. To determine if the source of this droop was carrier overﬂow, we plotted the peak energy and centroid energy against power density, as shown in Figure 5e. Typically, efﬁciency droop due to carrier overﬂow should be accompanied by a blueshift and broadening of the peak energy, since this implies migration to, and subsequent recombination of the carriers at, higher less localized energy states.\(^45,61\) However, no such blueshift was observed in the emission produced by the MQW structure under investigation; rather, the peak energy remained constant, as indicated by the blue-colored curve in Figure 5e. Furthermore, at a power density of \( \sim 10 \text{ MW cm}^{-2} \), the peak centroid energy red-shifted from 4.59 eV and settled at 4.53 eV, implying that the carriers had migrated to lower energy states. This peak shift can be attributed to the shift of the dominant recombination center from the high energy sub-QW states (4.59 eV) to low power densities to the main MQW states (4.53–4.55 eV).

To elucidate our ﬁndings further, we observe that the power dependence of the fwhm of the PL spectra, plotted in Figure 5f, initially broadens from \( \sim 102 \text{ meV} \) as the power density increases, and rapidly saturates at \( \sim 140 \text{ meV} \) (when the carrier density reaches \( \sim 10 \text{ MW cm}^{-2} \)). It is noteworthy that the onset of the efﬁciency droop effect coincides with that of the fwhm saturation, suggesting that the peak broadening is not linked to the droop effect. This result seems to rule out carrier overﬂow as the possible mechanism underlying the efﬁciency droop. As such, Auger recombination remains the most plausible loss mechanism in this TD-free MQW structure at high power densities.\(^62\) Nonetheless, it is worth noting that, as droop saturation occurred at a relatively high IQE (\( \sim 60\% \)), the radiative recombination processes effectively counteracted the droop mechanism. This counteraction process may have been aided speciﬁcally by the concurrent migration of carriers to the highly conﬁned low energy MQW states (4.55 eV) at high power densities.

To conﬁrm the origin of the droop, the log \( I_{PL} \) versus log \( G^k \) correlation for regions before and after the droop was analyzed, as shown in the inset of Figure 5d. According to eqs 1 and 2 for the injected carrier density range below the droop region (\( \leq 15 \text{ MW cm}^{-2} \)), \( k = 1.1 \) was obtained, conﬁrming that the emission is signiﬁcantly dominated by radiative recombination with negligible nonradiative recombination. On the other hand, \( k = 0.8 \) was obtained at carrier densities characterizing both droop and saturation regions (\( > 15 \text{ MW cm}^{-2} \)), which exceeds 2/3, indicating that the recombination process is governed by majority radiative recombination competing with minor Auger recombination process. This conﬁrms that the enhanced radiative recombination with minor Auger recombination stems from localized exciton in the sub-QWs. The numerical simulation conﬁrms the contribution of SRH and Auger recombination under low and high carrier injection modes, respectively (as shown in Figure S4 in Supporting Information). The analysis reported in this work can be applied to any semiconductor nanostructure system.
An AlGaN/AlGaN LED structure was homoepitaxially grown on a (0001) AlN substrate. HR-STEM cross-sectional and plan-view images revealed pseudomorphic, highly crystalline epilayers that are free from TD defects. The STEM and EDX measurements confirmed the presence of additional ultrathin sub-QBs and sub-QWs, caused by compositional pulling, which play significant roles in the carrier repopulation dynamics and the exciton localization, enhancing the efficiency and radiative recombination. Temperature- and power-dependent PL and TRPL, as well as results from numerical simulation measurements, revealed pseudomorphic, highly crystalline AlGaN/AlGaN MQW structures, which adds a potential degree of control in the quest for highly efficient DUV LED growth.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsphotonics.9b01814.

EDX atomic composition profile of Al$_{0.6}$Ga$_{0.4}$N/AlN superlattice layers, method for extracting PL carrier lifetime, information about DUV LED numerical simulation parameters, and additional analyses (PDF)

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Author Contributions
All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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