Temperature dependent carrier localization in AlGaInN near-ultraviolet light-emitting diodes

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Abstract: We investigate the carrier localization effect in the low-indium ultraviolet AlGaInN light-emitting diodes with a 365 nm peak and a wide yellow luminous band over the visible range. Temperature-dependent electroluminescence spectra (EL) are measured under a wide range of temperature. We found that carrier localization effect relies on the carrier mobility and manifests itself by altering several macroscopic quantities, such as ELs and electrical resistance of the device. Under moderate injection densities, plots of EL peak energy vs. temperatures exhibits S-shapes. At low temperatures, line-width broadening in EL spectra and irregular humps in I-V curves were observed at similar level of injection densities. Both phenomena diminish as temperature increases and eventually disappear at room temperature. All the results stem from carrier localization and following delocalization effect. It suggests that the carrier mobility determine the degree of carrier localization effect – inactive carriers tend to be localized at low temperature but escape at high temperature from bindings of localization centers. As a result, carrier localization is intense only at low temperature for low-indium devices.

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References and links

12. S. De, A. Layek, A. Raja, A. Kadir, M. R. Gokhale, A. Bhattacharya, S. Dhar, and A. Chowdhury, “Two distinct mechanisms have been proposed to account for the EQE droop, such as Auger recombination, nonradiative recombination via extended defects, and carrier leakage. At the same time, the EQE droop has caused considerable energy wastes. Several processes are responsible for the problem of low external quantum efficiency. The EQE depends on the injection density ($J_f$), a phenomenon is observed frequently in those high-indium devices, namely as the EQE droop [4]. Because the operating current usually corresponds to this region, the EQE droop has caused considerable energy wastes. Several mechanisms have been proposed to account for the EQE droop, such as Auger recombination [5], nonradiative recombination via extended defect [6], and carrier leakage [7,8]. At the moderate $J_f$, a phenomenon is observed frequently in those high-indium devices, namely the drop in EQE.


1. Introduction

The family of light-emitting diodes (LEDs) has been prosperous, since the moment when the feeble blue light was shining in Nakamura’s laboratory [1]. Various types of LEDs, which are made of III-V group elements and characterized by wide range of spectral from infrared to ultraviolet (UV), have hitherto been developed. Particularly, the GaN-based LEDs have received intensive researches owing to the surging of the market share of commercial available white high-power LEDs. Although the luminous efficiency of white LED realized by blue LEDs has exceeded 303 lm/W [2], the green and ultraviolet ones still suffer from low efficiency. Several processes are responsible for the problem of low external quantum efficiency (EQE). The EQE depends on the injection density ($J_f$) the device is being subjected to. What lies behind the processes is the interplay of carriers, point defects, extended defects and the lattice [3]. At low $J_f$, the dominant process is believed to be the well-known Shockley-Reed-Hall (SRH) recombination which is nonradiative through point defects (PDs) [4]. However, directly observation of the SRH recombination is difficult since the PDs themselves are un-luminous. With the increasing $J_f$, the SRH defect energy levels tend to be saturated and no longer function, resulting in the increase of EQE. After reaching the peak, the EQE falls down at higher $J_f$, namely as the EQE droop [4]. Because the operating current usually corresponds to this region, the EQE droop has caused considerable energy wastes. Several mechanisms have been proposed to account for the EQE droop, such as Auger recombination [5], nonradiative recombination via extended defect [6], and carrier leakage [7,8]. At the moderate $J_f$, a phenomenon is observed frequently in those high-indium devices, namely the
carrier localization effect, i.e. carriers are confined in local potential minima, which are usually associated with the indium segregation. For green InGaN LEDs that possess high indium composition, indium atoms tend to concentrate in some area in the active region, which results in local energy minima that will efficiently capture those approaching carriers. As a result, these localized carriers are prevented from being captured by those non-radiative recombination centers, therefore more likely to recombine radiatively at the band edge, than those non-localized ones [9,10]. Subsequently, the EQE in this $J_f$ region will increase. Moderate $J_f$ is required because at extremely low $J_f$, carriers are trapped by PDs before they reach any localization centers. Whereas, at extremely high $J_f$, these traps tend to be saturated by carriers, as a result, their ability to capture carriers diminishes, leading to the carrier delocalization effect, therefore a plunge in EQE can be observed [11,12]. However, it is still debatable whether or not the carrier localization effects play an essential role in the UV-LEDs where the indium composition is typically low [13–17].

![Diagram](image)

**Fig. 1.** (a) A sketch of the structure of the device under test; (b) the normalized EL spectra at 10 A/cm² for several temperatures ranging from 25K to 300K.

So far, tools in spectroscopy for identifying and evaluating the carrier localization is the temperature dependent PL, which typically exhibits an S-shape in the peak energy-temperature plot [14], and line-width broadenings when carrier localization occurs [15]. In our previous work, we analyzed the spatially resolved PLs, ELs and EQE-$J_f$ curves of the band-edge emission of blue LEDs, recorded at room temperature, and proposed that the delocalization effect results in a sharp plunge in the EQE at the initial stage of EQE droop [6]. In order to further study the carrier dynamics, it is necessary to extend the temperature of EQE curves measurement to low ones, at which thermal activation are omitted and some intrinsic properties of lattice are revealed [18,19]. In this work, we study the localization effect in low indium devices by employing several 365-nm UV-LEDs. Temperature-dependent EQE curves, ELs and I-V curves are measured. From the results we discover that the carrier mobility is pivotal for the carrier localization – At low temperature, as the carriers are inactive, the probability to be trapped in localization centers is higher than that at high temperature. We also find that in addition to line-width broadening in ELs, the carrier confinement will also temporarily increase the electrical resistance (compared with the prediction of Shockley equation) as well as the voltage drop of the active region. Whereas as delocalization occurs, the resistance deviation decreases thus the forward voltage reduces. This carrier-localization-induced resistance increase, to our knowledge, is observed for the first time. Both the spectral line-width broadening and resistance elevation diminish at higher temperature, indicating that the carrier localization effect is alleviated when carrier mobility is intense. Although generated from one sort of UV-LEDs, the understanding presented in the current paper are general over the wide-bandgap GaN-based devices, thus we believe that they will benefit the industry of solid-state lighting.
2. Experimental setup

The devices employed in this study are GaN-based UV-LEDs, of which the structures are illustrated in Fig. 1(a). As those typically vertical GaN-based devices, 10 pairs of AlInGaN/AlGaN multiple quantum wells (MQWs) serve as active region that are sandwiched between n-AlGaN and p-AlGaN layers grown on a c-axis sapphire substrate by metal-organic chemical vapor deposition. After growth, the wafer was bonding onto silicon substrate, and then processed into a 1 × 1 mm² vertical-structure LED chips after chip preparation. Chips are encapsulated without transparent lenses on top. We measure EL spectra of these devices under the temperature ranging from 25 to 300 K. A Keithley 2400 (Keithley Instruments Inc., USA) serves as the excitation source. The forward currents (\(J_f\)) for EL measurements, ranging from 0.5 to ~550 mA, correspond to \(J_f\) ranges from 0.05 to ~55 A/cm². The samples were cooled to 25 K using a closed-cycle helium refrigerator System (Advanced Research Systems Inc. USA). The spectra are detected by PMT-detector after being split by monochromator in conjunction with a Keithley 2611 (Keithley Instruments Inc., USA).

3. Experimental results and discussions

We measure the electroluminescence spectra (EL) at a series \(J_f\) under various temperatures down to 25 K. The ELs at 10 A/cm² are selectively illustrated in Fig. 1 (b), under several temperatures from 25 K to 300K. The ELs contain a main narrow UV peak located at ~365 nm (UVL), and a wide luminous band over the whole visible spectral range. Such yellow luminous (YL), having been observed both in EL and PL [13–17,20–23], received extensive studies for the past 30 years. Although its exact origin remains a puzzle, it has been associated with the PD emissions, e.g. Ga vacancies [22], carbon substitution defects [24], and the Co-N\(_2\)O complexes [25]. Nonetheless in this work we mainly focus on the UVL. As shown in Fig. 2(a), we plot the temperature dependent EQE curves, in which the EQE are calculated out of integrated intensity of the UVL band and the forward current. All the EQE data of different temperature are captured at the same experimental configuration, therefore, though absolute values of EQE are unknown, changes in relative intensity with temperature and \(J_f\) are well illustrated. With the increasing temperature, the overall EQE decreases as the droop onset (where the EQE reaches its peak in a droop curve) moves towards higher \(J_f\), from at ~1 A/cm² at 25 K to at ~10 A/cm² at 300 K, as shown in the yellow dash arrow. In the black line in Fig. 2(a), it is found that the EQE curve at 25 K exhibits a “spike” around the EQE peak, which gradually disappears with increasing temperature. Similar spikes can be seen in the local EQE curves of In-rich area in literatures, where they are interpreted as an evidence of the carrier localization and the following delocalization [6,7]. In fact, in the well-accepted ABC model [4], when the \(A\) coefficient, which is considered as the SRH recombination rate, is reduced, a
similar spike will generate at the EQE peak. The $A$ coefficient includes two aspects: non-radiative recombination rate $W_{nr}$ and the number of non-radiative recombination centers $N_{nr}$. On one hand, $N_{nr}$ can be effectively reduced due to carrier localization (if exists) at low temperature, and is increased with increasing temperature due to delocalization. A majority of carriers have been kept away from the non-radiative centers such as PDs in the case that they are confined by localization centers. Therefore, as revealed from the EQE curves and the ABC model, the localization effect may reduce $N_{nr}$, the effective density of SRH centers in consequence, resulting in higher EQE at low and moderate $J_f$. Those carriers localized within potential minima take place in the band-edge recombination, therefore the local EQE will be significantly enhanced. Whereas as the $J_f$ continues to increase, these potential minima are saturated and no longer trap newly injected carriers, which therefore have a higher probability of moving into nonradiative recombination centers, dramatically drawing down the EQE. The raising temperature also leads to such carrier delocalization – at higher temperature, carriers gain sufficient energy and escape from the localization centers. As a result, there are higher probability for them to be captured by non-radiative SRH centers than at lower temperature when they are localized, leading to increase in $N_{nr}$. Thus, the EQE increases slowly at higher temperature, and reaches its maximum at higher $J_f$ due to the enhanced effective PD density. The droop rate near onset $J_f$ could be utilized as a quantitative measure of degree carrier localization. We define the EQE droop rate in Eq. (1)

$$\xi = \frac{\eta_2 - \eta_1}{(I_1 - I_2)\eta_2}.$$  

In Eq. (1), $\eta$ denotes the EQE at the $I_f$ of its subscription $I_1$ and $I_2$. We only concern about the initial droop rate within the current range 20 mA after the droop onset, i.e., $I_2$ is set to at the droop onset, and $I_1$ is 20 mA larger than $I_2$. As illustrated in Fig. 2(b), the initial droop rate generally falls down with the increasing temperature, especially quickly at lower temperatures. According to previous discussions. The results in Fig. 2(b) may suggest that the carrier localization/delocalization effect become less intense at higher temperature. On the other hand, $W_{nr}$ can be thermally enhanced with an activation energy, but will be reduced and approach a constant but not zero at low temperature (because SRH recombination centers are still there), which is known as the defect frozen effect. As PDs subjected to extremely low temperature stop to function as non-radiative recombination centers, $W_{nr}$ decreases and carriers are more likely to participate in the band-edge recombination rather than SRH recombination. Therefore, no matter whether localization effect exists or not, such defect frozen effect leads to the decrease in $A$ coefficient at low temperature. Whereas, in the cases when localization exists, such $A$ coefficient decrease will be furtherly enhanced, since both $W_{nr}$ and $N_{nr}$ are together reduced by effects of defect frozen and localization respectively. In our work, as shown in Fig. 1(b), the ELs at lower temperature feature double peaks, of which the one with lower energy fades off as temperature increases. We consider it as a sign of localization effect. As a results, carrier localization at lower temperatures is at least part of the reason for the decrease in $A$ coefficient.

For more information, we investigate the ELs. As shown in Fig. 3(a), EL peak energies of UVL were recorded as a function of temperature. The energy band distortion by external electric field may be responsible for the phenomenon that peak energies all shift towards the red end as forward voltage increases. For the two lines with $J_f$ higher than 5 A/cm² but lower than 40 A/cm², with the increasing temperature, the peak energies firstly exhibit red-shift, followed by a blue-shift when temperature ranges from 50 to 100 K, and red-shift again as temperature rises to room temperature. As mentioned in the introduction section, this S-shape shifts in peak energy with the temperature, which is considered to be a result of carrier localization effect, has been widely reported in the PLs, but few in ELs. The first red-shift and the following blue-shift are associated with the carrier localization and delocalization respectively, and the second red-shift at higher temperatures is due to the bandgap shrinking induced by thermal expansion of lattice constants. It should be noted that the temperature of
the turning point from blue-shift to red-shift is as high as 100 K with \( J_f \) higher than 1 A/cm\(^2\). Such high temperature denotes that the carriers need large energy to escape from the localization, indicating a strong confinement effect in the localization potentials. No S-shape can be observed at the \( J_f \) lower than 1 A/cm\(^2\), which indicates the localization effect should depend on \( J_f \). At extremely low \( J_f \), the localization effect is minor since most carriers are captured by PDs before they are trapped by any localization centers. For the curve recorded at 40 A/cm\(^2\) where the carrier localization centers become saturated, the second blue-shirt fades, as the peak energies captured at 40 and 90 K are almost equal.

Fig. 3. (a) The temperature-dependent peak energy at different current densities; (b) FWHM vs. injection density at different temperatures; (c) I-V curves at different temperatures, arrows point out locations of humps at I-V curves with same color; and (d) The injection density dependent deviation of electrical resistance from the prediction of Shockley model, at various temperatures.

If the carrier localization can deter the peak energy of ELs, it should influence the line-width as well. To determine the onset \( J_f \) of localization effect, we plots the line-width of UVLs measured in full width at half maximum (FWHM) with respect to \( J_f \), as shown in Fig. 3(b). The black line of the lowest temperature of 25 K exhibits a surge that starts at ~2 A/cm\(^2\). Similar surges are found also in other temperatures, but with less degree. The line-width broadening is a clear sign of carrier delocalization effect – The localization centers serve as local energy minima, and they therefore emit photons with lower energy than those from normal band-edges while carriers recombine within them, respectively. As \( J_f \) increases, carriers start to delocalize and fill higher energy bands, which yields EL peaks with broader line-width. The value by which the line-width has increased corresponds to the degree of carrier localization. Therefore, the weakened surges at higher temperature reveal a reduced localization effect. It also can be found in Fig. 3(b) at levels of \( J_f \) below ~2 A/cm\(^2\), the FWHM increases with the temperature, and when the \( J_f > 2 \) A/cm\(^2\), this trend is inversed. At low injection levels, increasing temperature leads to a continuous increase of the spectra line-width is well known as the thermal broadening effects in the researches of localization effect. As the temperature increase, the band-filling effect in the deep localization center is dramatically enhanced due to the temperature-dependent intra-dot relaxation of the carriers. In
addition, the regular thermalization of carriers augments the line-width broadening at even higher temperatures, leading to a faster increase in FWHM. However, at high $J_f$ when delocalization is dominant, localization centers tend to be saturated, which leaves a homogeneous band-gap for newly injected carriers. In this case, as temperature increases, energy gap will shrink because of the Varshni's temperature dependence of bandgap. Thus, it results in a reduction in the peak energy as well as FWHMs.

The low temperature I-V curves are also recorded and presented in Fig. 3(c). The electrical resistance, defined as $R = V_f / I_f$, is associated with the mean carrier mobility – the higher carrier mobility, the lower the resistance. As the temperature increases, the I-V curve as a whole shifts downwards, due to the fact that increasing carrier mobility reduces the resistance. Interestingly, around 5 A/cm$^2$, near the onset $J_f$ of FWHM surges, each I-V curve recorded at below 40 K shows a "hump" (pointed out by arrows), where the voltages are larger than what the exponential model has predicted. For those I-V curves recorded above 90 K, no such hump is observed. At those V-humps, the resistance are higher than the prediction of Shockley model, indicating a reduction in mean carrier mobility. In Fig. 3(d), we plot the deviation in electrical resistance between experimental results and Shockley model, which clearly illustrates the resistance increase at temperatures lower than 90 K. The theoretical values are obtained from curve fitting of Shockley model. Comparing Figs. 3(b) and 3(d), we find that the surges in FWHM occur at $J_f$ levels higher than where resistance deviation located. Therefore we believe that carrier localization and following delocalization are their origins, respectively. When carriers are localized, their mobility is comparably lower than those non-localized ones. In those levels of $J_f$, at which carrier localization are dominant, a majority of carriers are localized, leading to lower mean carrier mobility and higher resistance than that of Shockley model. As $J_f$ increases, delocalization occurs, the numbers of non-localized carrier increases, raising the mean carrier mobility and draw the resistance back to the value of Shockley model. With increasing temperature, these irregular V-hump and the resistance departure gradually disappear, as the carrier localization/delocalization diminishes.

4. Conclusion
Combining the results presented above, via experimental results collected from the UV-LEDs with low indium composition, we are capable to present some principles of carrier localization effect. It requires both a sufficient number of localization centers and inactive carriers. Whereas in UV-LEDs, there are fewer sufficient localization centers due to low indium composition. Therefore, localization centers function only at very low temperature when the carriers are inactive and much easier to be captured. At higher temperature, the thermal activation of carriers is intense, resulting in a majority of carriers "vaporizing" out of the localization centers. Also, localization centers can be saturated at high injection levels. For both of these cases, the delocalization occurs. We also demonstrate that the carrier localization/delocalization effect can influence the photon energy distribution and the electrical resistance as well. When a large number of carriers are localized, the reduced carrier mobility leads to higher electrical resistance than theoretical prediction of Shockley model. With the increasing $J_f$, as carriers start to delocalize and occupy higher energy levels, the line-width of EL dramatically increases and the resistance returns to the theoretical value. Benefit from this property, we transfer the microscopic carrier localization to observable effects.

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