Study the Mechanisms of Enhanced Phonon Bottleneck Effect for the Absorber of Hot Carrier Solar Cell in III-V Multiple Quantum Wells

Yi Zhang¹ and Chao Huang²

¹ College of Energy and Electrical Engineering, Hohai University, Nanjing, China
² School of Electrical & Electronic Engineering, University of Manchester, UK
Email: zynjjs@outlook.com

Abstract. The most vital key to realize hot carrier solar cell is reducing carrier relaxation time to nanoseconds by phonon bottleneck effect often observed in nanostructure. However, the mechanisms underlying this are still not well understood. In this paper, we systematically investigated the mechanisms of phonon interfacial mismatch and carrier quantum confinement over phonon bottleneck effect in InN/InₓGa₁₋ₓN multiple quantum wells (MQWs). Highly promising hot carrier lifetimes due to enhanced phonon bottleneck effect were observed in these MQWs, where the longest hot carrier lifetime is 3.2±0.12 ns. It was found the quantum confinement of carriers could play more important role in the reduction of carrier cooling rate, while the optical phonon confinement is more likely to dominate the initial carrier temperature. This study clarifies two of the most important mechanisms of phonon bottleneck effect and directs a promising application of III-V MQWs on the absorber of hot carrier solar cell.

1. Introduction
The power conversion efficiency (PCE) of the single P-N junction silicon solar cells is restricted by Shockley-Queisser efficiency limit of 31%, making its highest PCE only 26.1% in one sun condition [1]. An alternative way to overcome this limit is to prevent thermalization energy loss by significantly reducing carrier cooling rate and utilize these hot carrier energy in time before the occurrence of complete thermalization. Such photovoltaic device concept is referred to as hot carrier solar cell (HCSC) which could potentially enhance its PCE upon to 66% in one sun condition [2, 3]. The key components of HCSC consist of a hot carrier absorber (HCA) sandwiched by two energy selective contacts (ESCs) [4], where the absorber aims to reduce carrier relaxation time to nanosecond time scale [5]. The quantum well structure has been proposed as candidate material for HCA via enhanced phonon bottleneck effect. The mechanisms underlying this effect seem to be due to either (1) large mismatch in optical phonon band at the interface between quantum well and potential barrier or (2) quantum confined effect for excited carriers, or both above. However, neither of them are well understood. The wurtzite InGaN alloy has the advantage that it could engineer both of its electronic and phononic band structures through adjusting the indium composition. The lattice mismatch between InN and InGaN could be well dealt with thin film growth technology called energetic neutral atomic-beam lithography/epitaxy molecular beam epitaxy (ENBALE-MBE) [6]. These make it possible to quantitatively investigate the mechanisms of phonon bottleneck effect in high quality InN/InGaN multiple quantum wells (MQWs).

In this paper, we study the two potential mechanisms mentioned above and clarify their relationship in InN/InGaN MQWs. Four InN/InₓGa₁₋ₓN MQWs samples with nominal indium compositions of x
value (i.e., InN mole fraction within InGaN) ranges from 25% to 75% were fabricated by ENABLE-MBE, where the width of quantum well ($L_W$) and that of potential barrier ($L_{PB}$) were maintained constant for all samples. Since the phononic band structures are changed due to variable $x$ values, which makes it possible to investigate confinement effect of optical phonon in these samples (i.e. mechanism 1). Additional two InN/In$_{0.25}$Ga$_{0.75}$N MQWs with different $L_W$ were also fabricated to investigate the quantum confinement effect of carriers within MQWs (i.e., mechanism 2). The crystallinity, phononic and optical properties of the samples were characterized by X-ray diffraction (XRD), cross-sectional transmission electron microscopy (cross-TEM) and steady-state photoluminescence (SSPL), respectively. The ultrafast carrier dynamics in picosecond time scale was studied by the femtosecond time-resolved photoluminescence (fs-TRPL). Power and wavelength of excited laser source in TRPL system are set to constant 100 mW/mm$^2$ and 400 nm, so that the effects of carrier density, intervalley scattering and dynamic carrier screening are eliminated. The phonon bottleneck effect could be reflected from hot carrier lifetime ($\tau_{hc}$) extracted from TRPL 2D contours. It was found both the confinement of optical phonons and that of carriers play role in extension of $\tau_{hc}$ and the longest one appears in the InN/In$_{0.25}$Ga$_{0.75}$N with $L_W$ of 5nm. Moreover, the confinement of carriers seems play more important role in terms of thermalization rate reduction, while that of optical phonon is able to significantly impact initial carrier temperature.

2. Experimental

2.1. Sample Fabrication

Four In$_x$Ga$_{(1-x)}$N/InN/In$_x$Ga$_{(1-x)}$N MQWs structure samples (i.e., sample A, B, C and D) with nominal $x$ value of 25%, 40%, 60% and 75% were grown by ENABLE-MBE on AlN substrate. The MQWs structure consists of 10 periods of 5nm InN wells embedded in 10nm InGaN barriers and is sandwiched by 20nm InN and 200nm GaN layers as buffer and reflector layers. Figure 1 demonstrates a schematic of the samples been studied in terms of physical and band structures. The thickness of each layer (especially for In$_x$Ga$_{(1-x)}$N) was carefully selected to minimize the effect of strain relaxation (i.e. thinner than their critical thickness) on carrier dynamics based on their composition. Additional two In$_{0.25}$Ga$_{0.75}$N/InN/In$_{0.25}$Ga$_{0.75}$N MQWs (i.e. sample E and F) were fabricated with $L_W$ of 10nm and 15nm, while keeping $L_{PB}$ 10nm unchanged. The details of these thin film growth can be found in Ref. [7].

![Figure 1](image1.png)

**Figure 1.** Schematic of an InN/In$_x$Ga$_{(1-x)}$N MQWs sample for HCA. The MQWs consists of InN well and In$_x$Ga$_{(1-x)}$N barriers, where $x$ ranges from 25% to 75%. This MQWs structure is sandwiched between two GaN buffer layers on AlN substrate. All thin film layers were grown by ENBALE-MBE.

2.2. Characterizations

The double-crystal XRD measurement was carried out by using a Philips PANa-lytical X’Pert PRO instrument with 0.1542nm Cu Kα radiation and PANalytical model software. The cross-TEM was employed by using the facility of Phillips, CM200. The SSPL measurement were conducted by using a 50mW 405nm excitation and a Si CCD camera for detection. A 442nm long pass filter was utilized to
remove the excitation light of the detector. The fs-TRPL experiments were implemented by a Clark-MXR laser CPA 2210 and fluorescence up-conversion spectrometer (i.e., Halcyone, Ultrafast System) with 0.64mm² spot size and 400nm excitation. The spot size was evaluated by imaging the laser spot. The details of the TRPL experiment has been described in Ref. [8]. All the experiments above were carried out at 300K.

3. Results and Discussion

Figures 2a-2d summarizes the 0-2θ XRD for Sample A-D, respectively. In these XRD spectra, the major peak assigned to the overlap of InₓGa₁₋ₓN and zero order satellite peak (SL-0) along with the first order satellite peak (SL-1) due to MQWs periodic structure were clearly observed, which indicates good quantum confined effect. The peaks at 31.3°, 34.6° and 36° are assigned to InN(0002) epitaxy layer, GaN(0002) buffer layer and AlN(0002) substrate, which are consistent with other work [9]. The SL-0 peak along with SL-1 peak shift towards lower 2θ degree with increasing x value, where the x value are close to design value within around 0.5-1% error based on the Vegard’s law. On the other hand, the thickness of each epitaxy layer within QW can be clarified by fitting the experimental X-ray diffraction spectra (blue line) to that of simulation ones (red line), indicating the actual thickness of each QW epitaxy is approximated to the designed values.

![Figure 2](image_url)

**Figure 2.** 0-2θ XRD spectra for sample A, B, C and D. The x value can be determined from XRD peak position which has a good agreement with the designed x value.

Figures 3 demonstrates the cross-sectional TEM images (scale bar = 5 nm) for Sample D-F with different nominal InN well widths (i.e., 5, 10 & 15 nm), where the InN well and InGaN barrier layers correspond to the bright and dark regions, respectively. The good crystallinity of all the samples are demonstrated according to the clear fringes observed in each epitaxy layers. In terms of InN epitax layer thickness, both of TEM and XRD experimental results are consistent with each other and approach to their nominal values.
Figure 3. Cross-sectional TEM for sample D, E and F, where each epitaxy layer thickness is indicated and clear fringes are observed.

Figure 4a presents the normalized infrared SSPL spectra for Sample A-D (i.e., Group #1) at room temperature. In each spectrum, it shows a major PL peak at -0.86eV assigned to the emission of InN quantum well ($E_W$) followed by a broad shoulder attributed to the emission of In$_x$Ga$_{1-x}$N potential barrier ($E_{PB}$). The In$_x$Ga$_{1-x}$N shoulders gradually shift towards longer wavelength with increasing $x$ value which is indicated by red arrow. It is believed that the MQWs PL spectrum is accumulated by that of InN and InGaN, thus a multi-Gaussian fitting is applied to PL spectrum to find the actual peak of InGaN. On the other hand, the FWHM (full width at half maxima) of InN peak is also studied to explore the quality of MQWs epitaxy layer. Figure 5b demonstrates the SSPL spectra for Sample D-F (i.e., Group #2) at room temperature for comparison, where both of $E_W$ and $E_{PB}$ shows a clear redshift with increasing $L_W$. An analysis similar to Group #1 was also conducted in this group. A summary of SSPL analyzed results for Sample A-F is show in table 1 where the theoretical results of InN and InGaN are in the parenthesis following their experimental results. The theoretical results of InN well peak are referred to the first quantum confined energy levels ($E_1$) in a finite potential well with effective width of $L_W$ (i.e., $L_{W_{eff}}$), where a schematic of quantum confined energy in finite QW is presented in the insert of figure 5a. The theoretical PL peak of InGaN barrier are calculated based on the Vegard’s law with a fully strained bowing parameter of 1.25. It indicates the $E_W$ of Sample A-F are closed to the calculated results, whose FWHM also are less than or similar to high quality InN MQWs in other research work [10]. However, the $E_{PB}$ for sample A-F are much smaller than the theoretical results due to the structural difference between bulk and quantum well.

Figure 5 gives an overview of 2D contours of TRPL for sample A-D. A clear blueshift of shoulder was observed with decreasing $x$ values of In$_x$Ga$_{1-x}$N barrier. Similar to SSPL spectra, the main peak corresponding to InN well remains unchanged at around -0.86eV. The carrier relaxation trends in all samples are indicated by the white arrows. All PL spectra at specific time delays extracting from TRPL could be modeled by a generalized Planck radiation law given by equation (1) below [15]:

![Figure 4. SSPL spectra of sample A, B, C and D are presented, which re-confirm the x values in terms of optical properties.](image-url)
Table 1. Summary of SSPL analysis results for MQWs samples.

| Sample | $E_W$ Exp.(Cal.) peak (eV) | $E_{PB}$ Exp.(Cal.) peak (eV) | FWHM of $E_W$ (meV) | Ref.    |
|--------|---------------------------|-------------------------------|---------------------|---------|
| A      | 0.87 (0.84)               | 0.99 (2.46)                   | 60.73               | [11-14] |
| B      | 0.86 (0.84)               | 0.97 (1.98)                   | 56.64               |         |
| C      | 0.85 (0.84)               | 0.93 (1.44)                   | 54.56               |         |
| D      | 0.86 (0.84)               | 0.91 (1.11)                   | 53.33               |         |
| E      | 0.80 (0.77)               | 0.87 (1.11)                   | 52.21               |         |
| F      | 0.73 (0.74)               | 0.79 (1.11)                   | 53.65               |         |

Figure 5. 2D contours of TRPL for A, B, C and D, indicating obvious reduction of carrier thermalization rate with increasing interfacial phonon mismatch between InN well and InGaN barrier.

$$I_{PL}(t) = \frac{A(\hbar \omega)(\hbar \omega)^2}{4\pi^2 \hbar^3 c^2} \left[ \exp(\frac{\hbar \omega - \Delta \mu}{k_B T_C}) - 1 \right]^{-1}$$

where $\hbar \omega$ is the emitted photon energy, $A$ is the absorptivity, $\Delta \mu$ is the chemical potential or quasi-Fermi-level separation under laser excitation, and $T_C$ represents the non-equilibrium hot carrier temperature at time delay of $t$. The $T_C$ along with temperature error at each time delay (i.e., $T_C(t)$) could hence be calculated to get an overview on hot carrier temperature variation trend. Then the carrier thermalization mechanisms could be reflected from carrier thermalization lifetimes ($\tau_i$) which can be extracted through a multiple-exponential Newtonian cooling model by the following equation:

$$T_C(t) = \sum_i T_{init} e^{-\frac{t}{\tau_i}} + T_{RT}$$

where $T_{init}$ represents the initial hot carrier temperature just after excitation (i.e. $t=0$ps), and $T_{RT}$ is the...
room temperature.

Figures 6a and 6b summarize the time dependent carrier temperature changing trend in logarithm and its key results for sample A-F. Extended carrier lifetimes ($\tau_{\text{overall}}$, the time excited hot carriers take to reach room temperature) greater than 3ns are observed in sample A-D due to phonon bottleneck effect. Sample A with the strongest phononic mismatch at the interface between InN well and InGaN potential barrier presents the highest $T_{\text{init}}$ of 1202±19K, while $T_{\text{init}}$ of sample D with the weakest interfacial phonon mismatch is only 651±15K. Since $E_1$ for sample A-D are the same, the quantum confined effect of them can be regarded as similar. These demonstrate the $T_{\text{init}}$ is strongly determined by the interfacial phonon mismatch rather than quantum confined effect, where a greater interfacial phonon mismatch could give a higher initial carrier temperature. This could be interpreted by that the optical phonons at interface are reflected back to InN well due to large interfacial mismatch, which makes it possible for these optical phonons to transfer their energy back to the excited carriers (i.e., “re-heat” the carriers in well). In terms of carrier lifetime, no evident change rule in $\tau_{\text{overall}}$ is found in sample A-D, which is possibly due to similar quantum confined effect. It could speculate that quantum confined effect may play a more significant role in the extension of $\tau_{\text{overall}}$. Therefore, sample D-F with increasing quantum well width (i.e. reducing quantum confined effect) and identical interfacial phonon mismatch (i.e., x value unchanged) are studied. Unlike previous samples with $\tau_{\text{overall}}$ greater 3 ns, $\tau_{\text{overall}}$ of sample E & F are only 936±80 and 452±120 ps, and their $T_{\text{init}}$ are 670±16K and 660±18K which is similar to that of sample D. These results confirmed the speculation that $\tau_{\text{overall}}$ and $T_{\text{init}}$ are primarily determined by the quantum confined effect and interfacial phonon mismatch via phonon bottleneck effect, respectively. Moreover, figure 7a shows a bi-exponential decay trend of carrier temperature in sample A-D and a mono-exponential decay trend of that in sample E-F. This implies that both mechanisms of interfacial phonon mismatch and quantum confined effect play role in sample A-D. However, only one mechanism does exist in sample E&F. Such mechanism is more likely to be the quantum confined effect, since the interfacial phonon mismatch in these samples are relatively weak according to the change of $T_{\text{init}}$ but the $\tau_{\text{overall}}$ in sample E&F are still much longer than that of other III-V bulk materials.

Figure 6. (a) A summary of time dependent carrier temperature for all MQWs samples from excitation to complete thermalization in picoseconds; (b) the schematic of two main mechanisms playing the role in hot phonon bottleneck effect during carrier thermalization process.

4. Conclusion

We quantitatively studied the two main mechanisms underlying the phonon bottleneck effect in InN/InGaN MQWs. A set of MQWs samples were fabricated by advanced ENABLE-MBE technology, which demonstrate good optical and crystallinity quality according to characterizations. The study on the ultrafast carrier dynamics according to TRPL indicates the quantum confined effect could effectively extend the carrier lifetime and the interfacial phonon mismatch is close related to the initial carrier temperature. The best sample A with x values of 0.25 shows the longest carrier lifetime of 3.2±0.12 ns
and highest initial carrier temperature of 1202±19K. The reduction of carrier cooling rate could be explained by the following processes. The excited carriers were firstly restricted at the first quantum confined energy level immediately after laser excitation. Then the emission of optical phonons from these carriers were reflected by the interfacial phonon mismatch back to quantum well. Since the main decay mechanism of optical phonons (i.e., Klemens decay) were prevented or even blocked by the overlap of great phonon bandgap and quantum confined effect in InN well, these reflected phonons are more likely to transfer their energy back to excited carriers and make contribution to the carriers re-heating. This is the first time to systematically study the mechanisms underlying the hot phonon bottleneck effect and the analysis give us a better understanding over the carrier cooling processes in MQWs. It also points out that direct bandgap III-V MQWs is one of the most suitable structure for HCSC absorber and other potential optoelectrical devices which required extended carrier lifetimes.

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