Efficiency dip observed with InGaN-based multiple quantum well solar cells

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Abstract
The dip of external quantum efficiency (EQE) is observed on In$_{0.15}$Ga$_{0.85}$N/GaN multiple quantum well (MQW) solar cells upon the increase of incident optical power density. With indium composition increased to 25%, the EQE dip becomes much less noticeable. The composition dependence of EQE dip is ascribed to the competition between radiative recombination and photocurrent generation in the active region, which are dictated by quantum-confined Stark effect (QCSE) and composition fluctuation in the MQWs.

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OCIS codes: (350.6050) Solar energy; (040.5350) Photovoltaic; (250.5590) Quantum-well, -wire and -dot devices; (160.2100) Electro-optical materials.

References and links

1. Introduction

The wide span of III-nitrides’ band gap ($E_g$), covering nearly the entire solar spectrum, has made the compound a promising material candidate for the next-generation photovoltaic devices [1]. The potential of nitride solar cells not only roots in the ideal values of $E_g$, but also the very high absorption coefficients ($>10^4$ cm$^{-1}$) in light of the compound’s direct $E_g$ [2,3]. In addition to these merits, nitride semiconductors exhibit many other favorable photovoltaic properties. For instance, their strong interatomic bonds and high thermal conductivities make the alloys suitable for high temperature operation [4], which is highly desired by concentrator solar cells. Moreover, the electrical and optical properties of In$\text{x}$Ga$_{1-x}$N exhibit very low sensitivity to high-energy proton irradiation, as compared with other well-developed solar materials (such as Si, GaAs and GaInP) [5]. The superior radiation resistance makes In$\text{x}$Ga$_{1-x}$N attractive for the applications in space photovoltaics.

In the design of device structure for nitride solar cells, MQWs are among the most adopted for the active region [6–14]. The popularity of MQW structure comes from two important considerations: i) the critical thickness of In$\text{x}$Ga$_{1-x}$N on GaN is less than 100 nm for...
x > 0.1 [15], but high indium contents are usually inevitable for a cell to absorb long-wavelength (λ > 450 nm) light. To avoid the trade-off between crystal quality and solar absorption, the MQW containing InGaN layers thinner than 10 nm is regarded as a feasible method for the active region. ii) Since the energy levels in a MQW structure is quantized, the absorption energy of the active region, being determinant to short-circuit current (J_sc), can be engineered not only by E_g of the wells, but also by the well widths. This extra manipulating dimension is further expanded by the notion that the open-circuit voltage (V_oc) of a MQW solar cell can be independently optimized by E_g (or the width) of the barriers, without changing the parameters of the wells [16]. Such decoupled control over J_sc and V_oc is not possible for conventional single-junction cells.

However, it cannot be over emphasized that the high radiative recombination efficiencies in a MQW structure could counter affect the generation of photocurrents. In a MQW solar cell, although the alternate wells and barriers offer additional freedoms in tuning J_sc and V_oc, the potential barriers of the MQW prevent electrons and holes from escaping the active region and thus lower the carrier collection efficiency. As a result, the loss of photocarriers through recombination, either radiative or nonradiative, is a vital factor in energy conversion efficiency, and should be taken into account when optimizing the device structure. The recombination dynamics is even more complicated in InGaN-based MQWs considering QCSE and indium segregation [17,18], both of which are the characteristics peculiar to InGaN thin layers because of the polarization-induced internal fields and the low miscibility of InN in GaN [19,20]. Yet, the correlation between carrier recombination and photocurrent generation in InGaN-based MQW solar cells is not well clarified to date.

In this letter, we report a direct observation of efficiency dip exhibited by InGaN/GaN MQW solar cells upon the increase of incident optical power densities. The efficiency dip is revealed by the MQW structure emitting blue light. However, for the MQW with green emission (by increasing indium contents), the dip effect is almost unnoticeable. The discrepancy is attributed to the different carrier dynamics in the well regions, dictated by QCSE and indium segregation. Detailed mechanisms responsible for the observed results will be explained.

2. Experiment

The MQW solar cells were grown by metalorganic chemical vapor deposition on c-plane sapphire substrates. Indium compositions of 15% and 25% were employed in the active regions. Both types of the MQWs are sandwiched by a 2.5-μm n-type (Si: 2 × 10^{18} cm^{-3}) GaN layer and a 0.2-μm p-type (Mg: 5 × 10^{17} cm^{-3}) GaN layer. The repeat of intentionally undoped In_{x}Ga_{1-x}N/GaN MQWs are 12 for x = 0.15 and 9 for x = 0.25 in consideration of lattice strain. In device fabrication, indium tin oxide (ITO) was deposited by electron beam evaporation on p-GaN to form transparent ohmic contacts. 1 × 1 mm² diode mesas were then defined by chlorine-based plasma etching. Ti/Al/Ni/Au metal grids were deposited on the ITO and n-GaN to serve as the electrodes.
Fig. 1. (a) PL spectra of the MQWs with 15% and 25% indium at the incident power density of 5 W/m². (b) PL peak wavelengths as a function of driving current for the MQWs with 15% and 25% indium.

3. Results and discussion

Figure 1 presents the photoluminescence (PL) spectra at the incident power density of 5 W/m² for the two In_xGa_{1-x}N/GaN MQW solar cells. It can be seen that the peak intensity from the MQW with 15% indium is around 1.6 times stronger than that from the MQW with 25% indium. Moreover, the full width at half maximum (FWHM) of the blue peak (15% indium) is only 60% of the other one. The stronger and narrower PL peak given by the 15%-indium MQW indicates a superior quality in carrier confinement. Increasing the indium content to 25% makes stronger the compressive strain exerted on the In_xGa_{1-x}N wells, which tends to create misfit dislocations in order to release the accumulated lattice tension [15]. The dislocations not only act as non-radiative recombination centers [21], but also smear out the well/barrier boundaries, making electrons and holes more likely to escape from the wells and/or recombine with deviated emission energies. Consequently, the PL performances deteriorate with increased indium contents.

QCSE can also affect carrier recombination in the MQW [17]. Figure 1(b) shows the PL peak wavelengths of the two solar cells with incident power density increasing from 5 W/m² to 25 W/m². The normalized full spectra can be seen in Figs. 2. The peak wavelength of the blue-emitting MQW is retained at 457.0 ~455.5 nm for all power densities, while that of the green-emitting MQW shifts from 537.0 nm at 5 W/m² to 533.0 nm at 25 W/m². The larger blue-shift of the green-emitting MQW is caused by the screening of QCSE [22]. The increased lattice strain with 25% indium leads to stronger piezoelectric polarization along the c-axis, and thus induces a larger internal electric field. The large internal field pushes electrons and holes towards the opposite sides in the wells, resulting in the lower radiative recombination efficiency and reduced recombination energies [22,23]. As more carriers are injected into the wells, the increased Coulombic force counterbalances the polarization-induced fields, restoring the flat-band condition, hence the blue-shift. The degree of QCSE and the aforementioned carrier-confinement qualities will be shown to play decisive roles in the quantum efficiencies of the MQW solar cells.
EQEs of the MQW solar cells with different indium compositions are presented in Fig. 3(a). The EQE shown here is defined as: \[ \text{EQE} = \left( \frac{J_{\text{op}}}{q} \right) / \left( \frac{P_{\text{op}}}{hv} \right) \], where \( J_{\text{op}} \) is the photocurrent density, \( q \) the electronic charge, \( P_{\text{op}} \) the optical power density, \( h \) Planck’s constant, and \( v \) the frequency of incident light [24]. In the figure, both of the solar cells exhibit the maximum efficiencies at \( \lambda = 380 \text{ nm} \). Similar observation was also reported by other groups [25–27]. The decreased EQE at the wavelengths below 370 nm indicates that the incident photons are absorbed in the MQW structure, instead of the p-type capping layer [27]. One can see that the EQE peak with 25% indium is lower, but wider than the one with 15% indium. The result is ascribed to composition fluctuation [7], crystal imperfections [28], and the hole-blocking band discontinuity in the active region of high indium contents [29], which have been thoroughly discussed in the cited references. Compared to those obtained with 15% indium, the lower EQEs with increased indium indicate lower \( J_{\text{sc}} \), which is shown by the J-V curves under air-mass (AM) 1.5G solar spectrum in Fig. 3(b). Table 1 lists the device characteristics determined from the figure.

![Fig. 2. Normalized PL spectra at the power densities from 5 W/m² to 25 W/m² for the MQW solar cells with the indium compositions of (a) 15%; (b) 25%.](image)

**Table 1.** The device characteristics determined from Fig. 3(b).

<table>
<thead>
<tr>
<th>In (%)</th>
<th>( J_{\text{sc}} ) (mA/cm²)</th>
<th>( V_{\text{oc}} ) (V)</th>
<th>FF (%)</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15%</td>
<td>1.65</td>
<td>2.30</td>
<td>63</td>
<td>1.52</td>
</tr>
<tr>
<td>25%</td>
<td>0.85</td>
<td>1.86</td>
<td>28</td>
<td>0.44</td>
</tr>
</tbody>
</table>

![Fig. 3. (a) EQE spectra of the two MQW solar cells with the incident power density at \( \lambda = 380 \text{ nm} \) fixed at 5 W/m². (b) J-V curves under AM 1.5G for the solar cells with 15% and 25% indium compositions.](image)
Figure 4 presents the peak EQE at 380 nm of the two solar cells with the incident power densities (at 380 nm) increasing from 5.0 W/m² to 6.1 W/m². The two solar cells exhibit very different photoelectric characteristics: the device with 25% indium shows increased EQE from 5.0 W/m² to 5.2 W/m² and remains fairly unchanged for higher power densities, whereas the one with 15% indium gains a little EQE initially, but loses noticeable efficiencies from 5.2 W/m² to 5.7 W/m² and picks up the EQE again afterwards. The distinctive EQE dip observed on the 15%-indium device can be analyzed with the rate equation in the MQW:

$$\frac{dn}{dt} = G - An - Bn^2 - Cn^3 - E$$

(1)

where $n$ is carrier concentration; G is the generation rate being proportional to the incident power densities; A, B, and C are the coefficients of Shockley-Read-Hall (SRH) nonradiative recombination, spontaneous radiative recombination, and Auger nonradiative recombination, respectively; E is the rate of carrier flow out of the quantum wells through thermionic excitation or insufficient quantum confinement, being contributive to the photocurrents (and thus EQE) of the solar cell. Equation (1) suggests that the rise and sink of EQE seen in Fig. 4 is dictated by the competition between E and the recombination terms (A, B, C). Since the excitation power densities during the measurement are very low, Auger recombinations within the MQW should be insignificant according to the studies by Shen et al. [30]. Further, it is believed that the SRH recombination, compared with radiative recombination, is less likely to cause the EQE sag seen in the figure. The premise is based on two considerations: i) as $n$ is increased by the higher excitation power density, the $n^2$ dependence of radiative recombination should make the term $Bn^2$ dominates over $An$ in Eq. (1). ii) If the defect-induced SRH recombination is the reason for the sink of EQE, the efficiency dip should take place in the MQW with higher indium content, i.e. 25%, whose $A$ coefficient is larger than that of the MQW with 15% indium because of the larger lattice mismatch between the well (InGaN) and the barrier (GaN). However, the EQE dip occurs in the MQW with 15% indium (fewer defect density), indicating that crystal defects are not the main culprit for the sagging efficiency.

![Fig. 4. The measured EQEs at $\lambda = 380$ nm as a function of incident power density for the two MQW solar cells.](image)

Summarily, the meandering of EQE with increased incident power can be explained with the simplified equation:

$$\frac{dn}{dt} = G - Bn^2 - E$$

(2)
A detailed mechanism can be visualized as follows: upon photo-illumination, electrons/holes are generated and confined in the quantum wells. The confined carriers can be further excited out of the wells, swept by the junction field, and collected by the electrodes, making contribution to EQE. Alternatively, the carriers can also be lost through radiative recombination, producing photons and thus resulting in the decreased EQE. Whether EQE is dominated by radiative recombination or photocurrent excitation is closely related to the dependence of B and E on indium composition of the MQW. In the quantum wells with 15% indium, carrier concentration rises when the incident power density increases, and the much more efficient radiative recombination [compared to the other device, as depicted in Fig. 1(a)] quickly consumes the confined carriers, giving rise to the EQE dip seen at 5.7 W/m². As the incident power density increases further, electron-hole pairs are continuously pumped into the wells and fill up the discrete energy levels, making it easier for the carriers to be excited out of the wells and thus adds more photocurrents, leading to the increased EQE.

Carrier dynamics in the MQW with 25% indium can be dramatically different. The increased indium composition results in severer QCSE, which greatly lowers the radiative recombination rate by spatially separating electrons and holes, making the $Bn^2$ term less competitive than $E$ in Eq. (2). Moreover, it has been found that increasing indium content in the MQW tends to induce compositional fluctuations in the $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy [18,20]. The indium fluctuation gives rise to the shallow quantum wells with the band gap energies close to that of the barriers. Carriers trapped in these shallow wells can be easily excited, either thermally or optically, over the barrier height, and generate additional photocurrents. Our studies with scanning transmission electron microscopy has revealed that the 25%-indium MQW contains much more shallow wells than the one with 15% indium [28]. The strong QCSE and inferior carrier confinement are believed to be the main factors leading to the less apparent EQE dip seen with the high-indium-content MQW.

In order to theoretically compare the EQE of the MQW solar cells, the output photocurrents from the two devices were calculated by solving self-consistent 1D Poisson and drift-diffusion equations [31]. In the calculation, an ideal MQW structure is assumed and QCSE is considered by setting the polarization-induced charges at the GaN/$\text{In}_x\text{Ga}_{1-x}\text{N}$ interfaces to $1.6 \times 10^{13}$ and $2.2 \times 10^{13}$ cm⁻² for $x = 0.15$ and 0.25, respectively [31]. SRH nonradiative carrier lifetime ($\tau_{nr}$) in the MQW is 150 ns for $x = 0.15$ and 110 ns for $x = 0.25$ [31]. Figure 5 presents the simulated EQE values at $\lambda = 380$ nm as a function of power density for the two solar cells. One can see the simulated EQEs for the MQW with 25% indium are higher than the measured values, which can be due to the unideal carrier collection of the real device. More importantly, the EQE curves of the two devices exhibit opposite trends as the power density increases. For the MQW with 25% indium, the EQE gradually increases with more incident photons, telling that carrier consumption in the quantum wells is dominated by photocurrent generation. On the other hand, the EQE with 15% indium decreases at higher power densities, indicating that the carrier loss due to radiative recombination outweighs photocurrent generation. Nevertheless, the EQE dip observed in Fig. 4 is not seen in the calculated results. One of the main reasons is the inhomogeneous distribution of indium composition in the MQW, which is not considered in the simulation and can significantly change the carrier densities in the MQW. As mentioned earlier, the immiscibility of InN and GaN usually leads to localized regions with the indium composition considerably higher or lower than the nominal value, and this can greatly influence the measured EQE values through the photocurrents generated from the localized regions. The randomly distributed indium fluctuation has been shown to play vital roles in carrier transport in InGaN-based MQWs and should be treated with sophisticated methods [32]. Although the measurement results are not fully repeated by the simulation, the presented theoretical analysis shows that the radiative recombination in the active region can adversely affect the EQE of InGaN/GaN MQW solar cells.
Fig. 5. Simulated EQE curves at $\lambda = 380$ nm as a function of incident power density for the MQW solar cells with 15% and 25% indium.

4. Conclusion

The dipping behavior of EQE exhibited by InGaN-based MQW solar cells is observed and theoretically analyzed. It is found the dip effect is apparent with the MQW containing 15% indium, and become less obvious when the indium percentage goes up to 25%. The result is attributed to two competing terms in the rate equation describing carrier dynamics in the MQW, i.e. radiative recombination and photocurrent excitation. The investigation presented here is an important step toward unfolding the photovoltaic behaviors of MQW structures.

Acknowledgments

The research was supported in part by National Science Council (102-2221-E-008-074, 102-2628-M-002-006-MY3 and 101-2221-E-002-115-MY2), National Taiwan University (103R7823), the Aim for the Top University Project of National Central University (103G903-2), and Energy Technology Program for Academia, Bureau of Energy, Ministry of Economic Affairs (102-E0606).