ABSTRACT

In recent year, InGaN-based alloy was also considered for photovoltaic devices owing to the distinctive material properties which are benefit photovoltaic performance. However, the Indium tin oxide (ITO) layer on top, which plays a role of transparent conductive oxide (TCO), can absorb UV photons without generating photocurrent. Also, the thin absorber layer in the device, which is consequent result after compromising with limited crystal quality, has caused insufficient light absorption. In this report, we propose an approach for solving these problems. A hybrid design of InGaN/GaN multiple quantum wells (MQWs) solar cells combined with colloidal CdS quantum dots (QDs) and back side distributed Bragg reflectors (DBRs) has been demonstrated. CdS QDs provide down-conversion effect at UV regime to avoid absorption of ITO. Moreover, CdS QDs also exhibit anti-reflective feature. DBRs at the back side have effectively reflected the light back into the absorber layer. CdS QDs enhance the external quantum efficiency (EQE) for light with wavelength shorter than 400 nm, while DBRs provide a broad band enhancement in EQE, especially within the region of 400 nm ~ 430 nm in wavelength. CdS QDs effectively achieved a power conversion efficiency enhancement as high as 7.2% compared to the device without assistance of CdS QDs. With the participation of DBRs, the power conversion efficiency enhancement has been further boosted to 14%. We believe that the hybrid design of InGaN/GaN MQWs solar cells with QDs and DBRs can be a method for high efficiency InGaN/GaN MQWs solar cells.

Keywords: InGaN multiple quantum well solar cells, quantum dots, luminescent down shifting, anti-reflection

1. INTRODUCTION

The InGaN-based alloys have been extensively used in light-emitting diode and laser diode. In recent year, InGaN-based alloy was also considered for solar cells application owing to the favorable photovoltaics properties such as direct bandgap, high absorption coefficient at band edge (on order of 10^5 cm^-1), high carrier mobility, superior radiation resistance, thermal stability [1-2], and, most important of all, the wide bandgap range of the InN/GaN alloy materials from 0.7eV to 3.4eV which covers almost all solar spectrum [3-4]. In addition, an over 60% in theoretical conversion efficiency of four-junction solar cells had been verified and the efficiency of tandem solar cells have been discovered to increase with the number of junction [5]. No matter how many junctions are contained in a tandem solar cell, it always requires junctions that possess bandgaps greater than 2 eV. However, very few materials possess bandgap over 2 eV [6]. InN/GaN alloy is one of the few materials that are adaptable under the criteria. Therefore, InN/GaN alloy can be a candidate for high efficiency tandem solar cell.

Nevertheless, there are still many challenges for InGaN-based photovoltaic devices. A large lattice mismatch between GaN and InN limits InGaN-based photovoltaic devices to have high indium composition active layer with large thickness for light absorption. Once the thickness of InGaN layer exceeds a critical thickness, there will be many unexpected
defects which lead to the recombination centers [7]. In general, the critical thickness of In$_{0.1}$Ga$_{0.9}$N is around 100nm, and decrease rapidly with increasing of indium composition [8]. The unexpected recombination centers increase the consumption rate of photo-generated electron-hole pairs further to degrade the photovoltaics performance. Due to crystal quality concern, although multiple quantum wells (MQWs) structure is suitable for solar cell absorber, the thin quantum-well absorber restricted by the epitaxial challenges has led to insufficient light absorption [9]. On the other hand, indium tin oxide (ITO) is usually deposited as a conducting and transparent layer, however ITO shows a high absorption coefficient at ultraviolet region without generating photocurrent. Therefore, a new approach for solving the insufficient light absorption and reducing the high absorption of ITO layer is needed to be developed.

In previous studies, there are many approaches demonstrated to improve the light harvesting of InGaN MQW solar cells, such as using ZnO or SiO$_2$ sub-wavelength structure to realize the graded refractive index interface for reduction of Fresnel reflection, and simultaneously, for achievement of light scattering effect [10]. In addition, silver nanoparticle was used to utilize the surface plasmonic effect further to increase light scattering effect [11]. However, both of the issues of high absorption at ultraviolet region due to ITO layer and the low external quantum efficiency due to the insufficient light absorption has not been solved. Back reflector which reflects the unused light back to the absorber layer can play an important role in thin film solar cells [12]. The advantages of distributed Bragg reflectors (DBRs) include high reflectance, controllable stop band, and controllable central wavelength. By choosing appropriate DBRs, the issue of low external quantum efficiency can be solved. In the past, QDs have been widely used in optoelectronic devices such as light emitting diodes (LEDs) and solar cells. Recently, the CdS quantum dots on the top of the solar cell device with luminescent down shifting (LDS) effect and anti-reflective characteristic has been demonstrated [13-14]. The luminescent down shifting effect can absorb light in ultraviolet region and emission the light into longer wavelength, thus the issue of high absorption at ultraviolet region of ITO layer can be solved.

In this work, we successfully demonstrated a hybrid design InGaN/GaN MQWs solar cells utilizing colloidal CdS QDs and back-side DBRs to enhance the light harvesting of InGaN/GaN MQWs solar cells. The characteristics of InGaN/GaN MQWs solar cells with colloidal CdS QDs and back-side DBRs were measured by reflectance spectra, external quantum efficiency (EQE), and current density-voltage (J-V) profile.

2. EXPERIMENT

The InGaN/GaN MQW solar cell were grown by Metal-organic chemical vapor deposition (MOCVD) on c-plane sapphire substrate. The devices were composed with a 30-nm thick low temperature GaN nucleation layer and a 2-$\mu$m thick undoped GaN on sapphire substrate, 14 pairs In$_{0.15}$Ga$_{0.85}$N/GaN (3nm/5nm) undoped MQW sandwiched by a 2-$\mu$m thick Si-doped n-GaN layer (n-doping=2×10$^{18}$ cm$^{-3}$) and a 200-nm thick Mg-doped p-GaN (p-doping=2×10$^{17}$ cm$^{-3}$). A 110-nm thick indium-tin-oxide (ITO) p-GaN conducting layer was deposited by sputtering system. And then, the device were defined by 2x2 mm$^2$ mesa using inductively coupled plasma reactive ion etching (ICP-RIE) system. Finally, Cr/Pt/Au (50/50/1900nm) was deposited by electron-beam evaporation which serves as the p-GaN and the n-GaN contact metal.

The distributed Bragg reflector were composed of 11 pairs HfO$_2$/SiO$_2$ and grown by sputtering system at room temperature and deposited on the glass substrate. For controlling central wavelength and stop band of DBRs, the quartz was used to monitor during the process. Fig. 1(b) shows the measured reflectance spectra of 11 pairs HfO$_2$/SiO$_2$ DBRs, from wavelength of 385nm to 460nm, the reflectance is over 98%.

After regular semiconductor processes, the spin-coating method was used to form a CdS quantum dots thin film on the top of the device and DBRs was put at the back side of the device. The entire device structures are shown in Fig. 1(a).
Figure 1. (a) Schematic of InGaN/GaN MQW solar cell structure with CdS QDs and DBRs. (b) The measured reflectance spectra of 11 pairs HfO2/SiO2 DBRs.

Fig. 2(a) shows the absorbance and photoluminescence spectrums of CdS QDs in toluene. In absorbance spectrum, a sharp rising edge was detected around 400nm and the peak absorption occurred at around 380nm. The photoluminescence spectrum was measured by the 365 nm excitation, and a major emission wavelength is around 410 nm. Fig. 2(b) shows the scanning electron microscopic (SEM) image of the CdS QDs on the top of InGaN/GaN MQW solar cells. We can observe the nanosphere-like structure on the surface which were the self-assemble CdS QDs clusters and the diameters are around 80–100nm. Four kinds of InGaN/GaN MQW solar cells are prepared for analysis: one with CdS QDs, one with DBRs, one with both CdS QDs and DBRs, and one bare cell as reference.

Figure 2. (a) The measured photoluminescence (blue) and UV-Vis absorbance (black) spectra of CdS QDs in toluene. (b) The scanning electron microscopic (SEM) image of the CdS QDs on the top of InGaN/GaN MQW solar cells.

3. RESULT AND DISCUSSION

The reflectance spectra of the InGaN MQW solar cell with CdS QDs, the cell with DBR, the cell with both CdS QDs and DBRs, and the reference bare cell are shown in Fig. 3(a). When comparing the reflectance spectra of the cell with and without QDs, the reflectance spectra illustrate that CdS QDs provide a significant broadband anti-reflection characteristic. The anti-reflection characteristic of CdS QDs can be caused by light scattering effect of the nanosphere-like CdS QDs clusters. In addition, because the wavelengths of incident photons are larger than the dimension of the nanosphere-like CdS QDs clusters, according to the effective medium theory, these clusters provides a graded refractive index interface and resulting in broadband anti-reflection characteristic for light harvesting [21].
Figure 3. The measured reflectance spectra of InGaN/GaN MQW solar cell with CdS QDs, the cell with DBR, the cell with both CdS QDs and DBRs, and one bare cell as reference.

The measured photovoltaic current density-voltage (J-V) curves of the four types of InGaN/GaN MQW solar cells were performed under a simulated AM1.5G illumination condition and the results are shown in Fig. 4(a). The details of measured results are listed in Table 1. Compared to the reference cell, the short circuit current density ($J_{SC}$) enhancement of the cell with only CdS QDs and the cell with only DBRs are 5.5% and 16.5% respectively. With the combination of CdS QDs and DBRs, the enhancement in short circuit current density can be further boosted to 22%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>F.F. (%)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>1.35</td>
<td>1.09</td>
<td>56.03</td>
<td>0.83</td>
</tr>
<tr>
<td>QDs</td>
<td>1.34</td>
<td>1.15</td>
<td>54.52</td>
<td>0.85</td>
</tr>
<tr>
<td>DBR</td>
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<td>1.27</td>
<td>56.19</td>
<td>0.98</td>
</tr>
<tr>
<td>QDs+DBR</td>
<td>1.37</td>
<td>1.33</td>
<td>54.79</td>
<td>1.002</td>
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</table>

Table 1. Current-Voltage Characteristics of InGaN/GaN MQW solar cell with CdS QDs, the cell with DBR, the cell with both CdS QDs and DBRs, and one bare cell as reference.

Fig. 4(b) shows the measured external quantum efficiency (EQE) of the four types of InGaN/GaN MQW solar cells. The results of EQE can indicate the relationship between light absorption and photocurrent. The low EQE at the wavelengths shorter than 360nm can be attributed to several reasons, including junction depth, surface recombination, and absorption of ITO layer at UV regime. For the cell with only CdS QDs, there exhibits an overall EQE enhancement at a wavelength ranging from 350 nm to 440 nm which can be attributed to light scattering effect and anti-reflective characteristic of the nano-cluster CdS QDs on top. The results well agree with the reflectance spectra. It is noteworthy that, a significant enhancement at a wavelength ranging from 350 nm to 365 nm is observed from EQE of the cell with CdS QDs when comparing to that of reference cell. It is due to down conversion capability possessed by CdS QDs. As UV photons incident into the cell with CdS QDs on top, instead of being absorbed by ITO, they are absorbed by CdS QDs and then be converted into photons with longer wavelengths, therefore are able to penetrate through ITO layer without absorption and reach MQW absorber layer. To avoid incident photons being absorbed in ITO layer can suppress deterioration in EQE brought by the poor photon-generated carrier extraction efficiency of ITO and surface recombination in ITO layer. For the cell with only DBRs, there shows a significant EQE enhancement at a wavelength range of 380- 440 nm due to that the DBRs can reflect the photons back into MQW absorber layer and prolong the
optical path length further to enhance the absorption. By combining the CdS QDs and DBRs, the EQE shows a significant broadband enhancement at a wavelength range of 350–440 nm. Compared to other three kinds of cell, the cell with both CdS QDs and DBRs shows the highest EQE which transforms into the highest JSC.

Figure 4. (a) The measured photovoltaic current density-voltage (J-V) curve (b) The measured external quantum efficiency (EQE) of InGaN/GaN MQW solar cell with CdS QDs, the cell with DBR, the cell with both CdS QDs and DBRs, and one bare cell as reference.

To further understand the influence of CdS QDs on the InGaN/GaN MQW solar cells, detail analysis in EQE and absorption is introduced in the following. Fig. 5 shows the enhancement factors of both EQE and absorption of the cell with CdS QDs when comparing to reference cell. The enhancement in absorption of the longer wavelength is achieved by AR characteristic of the CdS QDs, not the LDS effect of CdS QDs. A significant peak at a wavelength range of 350–365 nm can be observed in EQE. The difference between CdS QDs absorption spectrum and EQE enhancement can be explained by the LDS of CdS QDs. Most of UV-photon-generated electron-hole pairs in solar cells are located near the surface which can be severely affected by the surface defects. The presence of CdS QDs can re-emit photons with longer wavelengths and reduce the influence of surface defects and ITO layer. In Fig. 5, a strong enhancement peak around 360 nm indicates the improvement brought by this CdS QD layer.

Figure 5. The enhancement factors of both EQE (blue line) and absorption (red line) of the cell with CdS QDs when comparing to reference cell.
4. CONCLUSION

We successfully demonstrated a hybrid design of InGaN/GaN MQWs solar cells combined with colloidal CdS QDs and back side DBRs. The down-conversion and anti-reflective effects of CdS QDs enhance the EQE for light with wavelength shorter than 400 nm, and the back side DBRs have effectively reflected the light back into the absorber layer which result in a broad band EQE enhancement. Finally, the overall power conversion efficiency enhancement as high as 7.2% compared to the device without assistance of CdS QDs. With the participation of DBRs, the power conversion efficiency enhancement has been further boosted to 14%.

REFERENCES