Linear photon up-conversion of 450 meV in InGaN/GaN multiple quantum wells via Mn-doped GaN intermediate band photodetection

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Abstract: Up-converted heterostructures with a Mn-doped GaN intermediate band photodetection layer and an InGaN/GaN multiple quantum well (MQW) luminescence layer grown by metal-organic vapor-phase epitaxy are demonstrated. The up-converters exhibit a significant up-converted photoluminescence (UPL) signal. Power-dependent UPL and spectral responses indicate that the UPL emission is due to photo-carrier injection from the Mn-doped GaN layer into InGaN/GaN MQWs. Photons convert from 2.54 to 2.99 eV via a single-photon absorption process to exhibit a linear up-conversion photon energy of ~450 meV without applying bias voltage. Therefore, the up-conversion process could be interpreted within the uncomplicated energy level model.

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1. Introduction

Recently, various attempts have been made to improve the efficiency of solar cells by exploiting intermediate band absorption and up-conversion effects. These processes transform additional low-energy photons in the solar spectrum into high-energy ones [1–6]. Up-converter devices that absorb low-energy photons and emit high-energy ones by electron-photon and -phonon interactions invariably consist of two components, one for photodetection and another for luminescence. Several types of up-conversion methods have been investigated, including second-harmonic generation [7], two-step two-photon absorption process involving quantum dot states [8, 9], and internal photoemission from a Schottky contact [10, 11]. An intermediate band material that has a partially filled impurity energy band in the host semiconductor band gap can absorb photons with energies lower than this band gap. There are many possible intermediate band semiconductors, such as the transition-metal-doped compounds GaP [12], ZnS [13], ZnTe [14], and GaN [6, 15,16]. These compounds have wide band gaps that provide a higher possibility of intermediate band formation. Many theoretical and experimental investigations conducted on Mn-doped GaN have shown that deep Mn impurity bands could form in the band gap of GaN. Moreover, the energy level (impurity band of $Mn^{2+/3+}$) introduced by Mn in GaN is located approximately in the middle of the GaN bandgap [15–22]. Mn-doped GaN materials have been used as diluted magnetic semiconductors in the field of spintronics. However, the intermediate band characteristics of Mn-doped GaN up-converter devices have seldom been reported [23–26].

In principle, the up-conversion photoluminescence (UPL) phenomenon requires a mechanism that up-converts electrons and/or holes from the low- to the high-band-gap material. Relaxation back into the low-band-gap material must not occur before the carriers radiatively recombine in the high-band-gap material. In other words, low-energy

photogenerated carriers should be moved away from the low-band-gap material layer, and the carriers should eventually be radiatively recombined in the high-band-gap material layer. Mn-doped GaN can be a potential candidate for the up-converted photodetection given its intermediate band absorption characteristics. In the present paper, we designed an up-converter based on a homologous GaN-based material system. The up-converters consisted of Mn-doped GaN intermediate band materials for photodetection, and InGaN/GaN multiple quantum well (MQW) structures for radiative luminescence. Low-temperature UPL and room-temperature spectral responsivities were obtained from these heterostructures. Hence, the UPL was mainly attributed to the fact that low-energy photons generated electrons from the Mn-doped GaN layer. These photons were then injected into the InGaN/GaN MQWs, leading to the UPL. Details regarding the UPL mechanism were discussed.

2. Device fabrication and experiment methods

Samples used in the present study were all grown on c-face sapphire substrates by metallorganic vapor phase epitaxy. The epitaxial layers of up-converter samples were labeled as sample A. The structure of the samples consisted of 6 layers. First was a 30 nm-thick GaN nucleation layer grown at 560 °C. Second was a 3 μm-thick unintentionally doped GaN (u-GaN) template layer grown at 1060 °C. Third was a 1 μm-thick Mn-doped GaN up-converted photodetection layer grown at 1010 °C. Fourth was a 0.2 μm-thick Si-doped *n*-GaN layer grown at 1040 °C. Fifth was a 10-pair InGaN-GaN MQW structure luminescence layer grown at 770 °C. Sixth and last was a 0.2 μm-thick u-GaN cap layer grown at 950 °C. The Mn dopant concentration was on the order of 10^{20} cm^{-3} as determined by secondary ion mass spectrometry. Samples without an Mn-doped underlying layer were also prepared and labeled as sample B for comparison. The electron concentration of the Mn-doped GaN was well below 10^{16} cm^{-3}. Hence, the 0.2 μm-thick *n*-GaN ($n = 5 \times 10^{18}$ cm^{-3}) layer may be able to enhance the injection of photo-generated carriers from the Mn-doped GaN layer to the InGaN/GaN MQWs. This enhancement may be achieved via the internal electric field formed at the step-doping junction (undoped/Si-doped junction). In addition, GaN samples with and without Mn doping layers, which were labeled as samples C and D, respectively, were grown at 1010 °C. Figure 1 shows the schematic layer structures of samples A, B, C, and D. To evaluate the effect of Mn doping in GaN on the spectral responsivities, a series of procedures (including photolithography, plasma etching, and metallization techniques) were performed on samples C and D. These procedures caused the formation of electrodes on the samples behaving as photodetectors [27]. The UPL measurements of the samples were performed at 12 K. The excitation sources were an He-Cd laser at 325 nm and an Ar laser at 488 nm. The UPL signal was dispersed by a monochromator (Acton SP-500), and was detected by a thermoelectrically cooled photomultiplier tube (Hamamatsu R94302) using the photon counting method. The responsivities of the samples were measured by combining an HP 4156C semiconductor parameter analyzer with a 300 W Xe arc lamp and a calibrated monochromator used as light source.

3. Results and discussion

Figure 2(a) shows the typical PL spectra of samples A and B excited by a 325 nm He-Cd laser. The spectra taken from samples A and B both had weak emission peaks at around 353 nm (3.51 eV) and a strong emission peak at around 415 nm (2.99 eV) that corresponded to the

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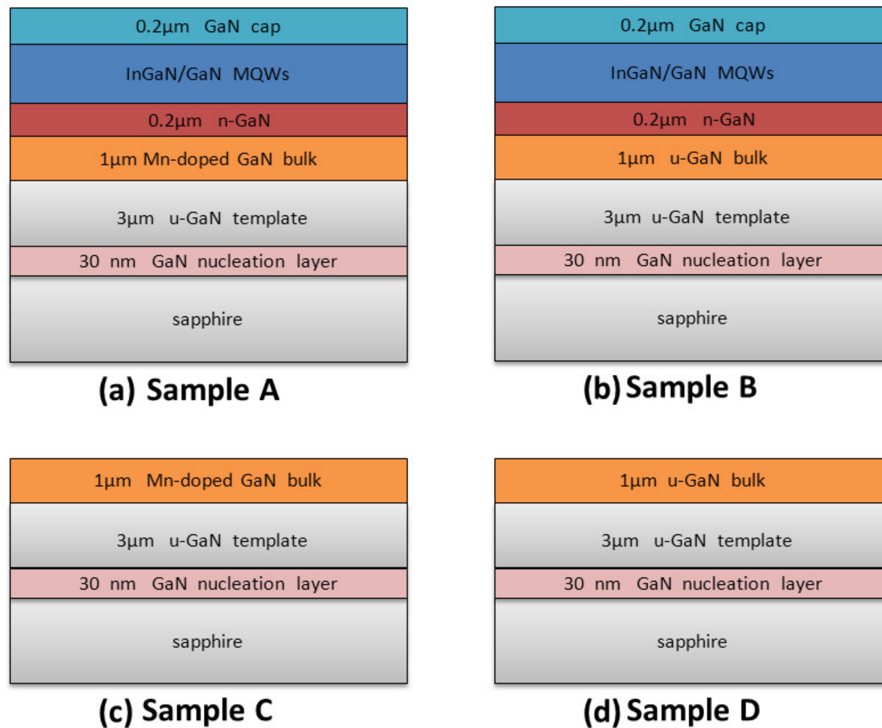

Fig. 1. Schematic device structure in cross-section view: (a) samples A, (b) samples B, (c) samples C and (d) samples D.

GaN layers and the InGaN QWs, respectively. Figure 2(b) shows the typical PL spectra of samples A and B excited by a 488 nm Ar laser (E_{exc} = 2.54 eV). No emission peak was observed from sample B due to the excitation photons with energies lower than the band gap of the GaN layers and InGaN QWs. However, the PL spectrum taken from sample A exhibited two peaks at 2.99 and 3.51 eV. The emission peak energies were all higher than the photon energy of the excitation light source (2.54 eV). Hence, this result implied that an up-conversion process can be achieved by the prepared InGaN/GaN heterostructures with a Mn-doped GaN photodetection layer. To clarify further whether the emission peaks of sample A were due to the up-conversion process, two designed samples [Figs. 1(c) and 1(d)] were also excited by a 488 nm Ar laser (2.54 eV) to evaluate their PL spectra. As shown in Fig. 3, the PL spectrum of sample C had weak and broad emission peaks at around 3.1–3.2 eV. In contrast, the emission peak of sample D was almost undetectable. The broad band emission of sample C could be due to the transition of the Mn-related impurity band in the Mn-doped GaN layer. Graf et al. [22] reported that a donor level with an energy of around 0.3 eV above the valence band could be formed by Mn doping in the GaN layer. Therefore, the emission at around 3.1–3.2 eV could be attributed to the transition of electrons in the conduction band to the Mn-related donor states near the valence band. On the other hand, peaks at 2.99 and 3.51 eV were not observed from samples B, C, and D, as shown in Fig. 3. The strong emission peak at 2.99 eV from sample A could be attributed to two possible excitation sources. One is a photo-injection from the Mn-related emission in the Mn-doped GaN bottom layer at peak position from around 3.1–3.2 eV. The other is an electrical injection from the up-converted photo-carriers generated in the Mn-doped GaN layer to the InGaN QWs. The weak but sharp emission peak at 3.51 eV of GaN in sample A was also observed, as shown in Fig. 3. Considering sample A, the origin of its characteristic GaN PL peaks [Figs. 2(b) and 3] should

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be different from those in Fig. 2(a). This difference attributed to the fact that the excitation source energy of 488 nm (Ar laser) was lower than the peak GaN PL energy. This result indicated that the peak GaN PL was not due to the photo-injection from the Mn-related broad emission for the excitation of the GaN layers. Therefore, the characteristic GaN PL peak displayed in Fig. 3 was most likely due to the electrical injection from the up-converted photo-carriers generated in the Mn-doped GaN layer. In other words, electrons were pumped from the Mn-related impurity band to the conduction band of the Mn-doped GaN layer. A part of the pumped electrons subsequently injected to the conduction band of MQWs led to the emission peak at 2.99 eV. On the other hand, another part of the electrons fell down to the valence band of the *n*-GaN spacer layer and led to the emission peak at 3.51 eV.

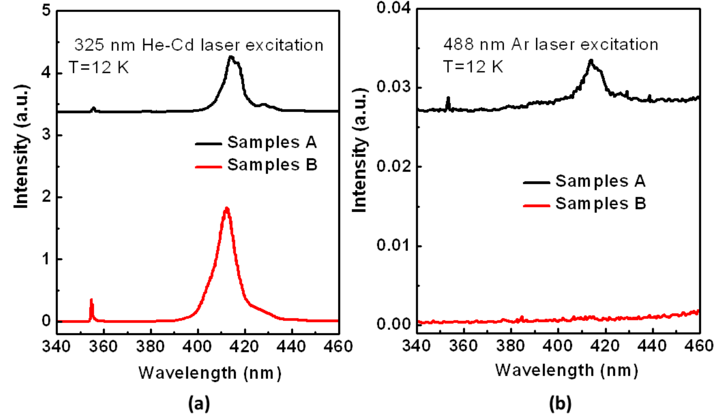

Fig. 2. Low temperature (12 K) PL spectra of samples A and B for the indicated (a) 325 nm He-Cd laser excitation and (b) 488 nm Ar laser excitation.

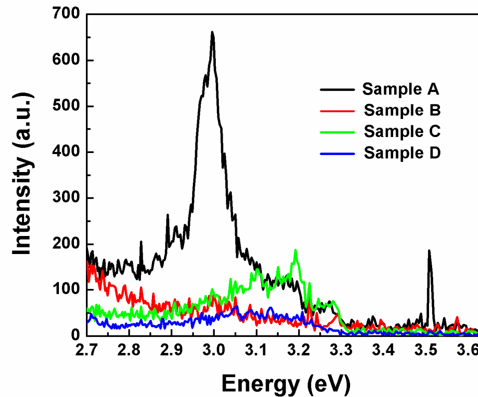

Fig. 3. Low temperature (12 K) PL spectra for the 488 nm (2.54 eV) Ar laser excitation of samples A, B, C and D.

To explore further the origin of the up-conversion process, the Schottky photodetectors PD-I and PD-II were created from samples C and D, respectively. These photodetectors were characterized at room temperature (300 K) and zero bias to evaluate their spectral responsivities. As shown in Fig. 4, PD-II (with an undoped GaN absorption layer) exhibited only a typical sharp transition at around 3.4 eV (i.e., the bandgap of GaN at room temperature). On the other hand, PD-I exhibited a clear two-step photoresponse. The broad below-band-gap response (1.9–3.1 eV) could be attributed to the fact that the electrons were

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excited from the Mn impurity band and Mn-related structural defect states in the bandgap of the Mn-doped GaN layer to the conduction band. The carriers generated from the Mn impurity bands were subsequently transported through the GaN layers, and were eventually collected by the external electrodes to exhibit the below-band-gap response. In other words, these broad- and below-band absorptions indicated that the strong emission peak at 2.99 eV from sample A [Figs. 2(b) and 3] was most likely due to the electrical injection of the up-converted photo-carriers. These photo-carriers were generated by the absorption of the Ar laser at an energy of 2.54 eV in the Mn-doped GaN layer. The carriers were subsequently transported through the *n*-GaN spacer layer to the InGaN/GaN MQWs. Consequently, a strong up-conversion emission of the peak at 2.99 eV and a weak peak at 3.51 eV occurred. As aforementioned, the below-band-gap response was due to the collection of photo-carriers generated by the intermediate band absorption. This finding indicated that Mn-doped GaN has potential use in up-converted photodetection using III-nitride semiconductors.

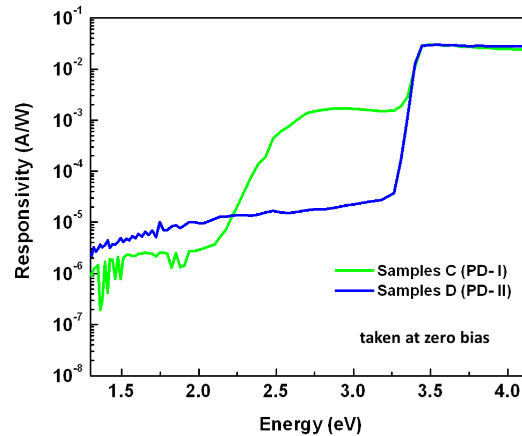

Fig. 4. Typical room temperature (300 K) spectral responsivity of the PD-I(sample C) and PD-II(sample D) taken at zero bias.

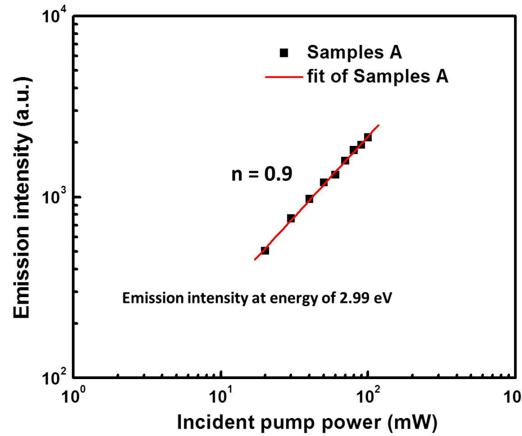

Fig. 5. 488 nm (E_{exc} = 2.54 eV) Ar laser incident pump power dependence of the spectrally up-converted PL emission intensity of samples A at low temperature (12 K). The lines show the linear regression in the double-logarithmic plot. The slope of n = 0.9 is also indicated.

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These above experimental results have provided tentative evidence that the UPL emission peaks at 2.99 and 3.51 eV were due to the injection of photo-carriers from the Mn-doped GaN layer to the InGaN/GaN MQWs. For practical applications such as an efficient photovoltaic device, discovering how to enhance the injection efficiency of up-converted photo-carriers from the Mn-doped GaN layer to InGaN/GaN MQWs is essential. However, the design of a UPL-efficient device should be based on an insight into the mechanism of carrier dynamics. To understand further the UPL emission mechanism in sample A, a power-dependent PL analysis was performed. The slope of a double-logarithmic plot of emission intensity (at a given energy) versus excitation power was evaluated. This method is commonly used to investigate power dependence for obtaining insight into up-conversion mechanisms. Figure 5 shows the integrated PL intensity at a given energy of 2.99 eV as a function of excitation power of the 488 nm (E_{exc} = 2.54 eV) Ar laser. Based on a linear regression of the double-logarithmic plot, a slope of n = 0.9 was obtained. The emission intensity of QWs excited by both photo-injection and electrical injection methods is known to be linearly proportional to the excitation power. In other words, the slope of n = 0.9 implied that the proposed UPL mechanism was a single-photon excitation process. In other words, the integrated UPL signal intensity was almost linearly dependent on the excitation power of the laser with an energy (2.54 eV) lower than the material band gap (2.99 and 3.51 eV). These results indicated that the intermediate band absorption of the Mn-doped GaN photodetection layer excited by 2.54 eV photons was a single-photon absorption process. This process involved electron transitions from the Mn-impurity band to the conduction band. These findings were consistent with the spectral responses obtained from PD-I, as shown in Fig. 4, and can be interpreted by the uncomplicated energy level model, as shown in Fig. 6.

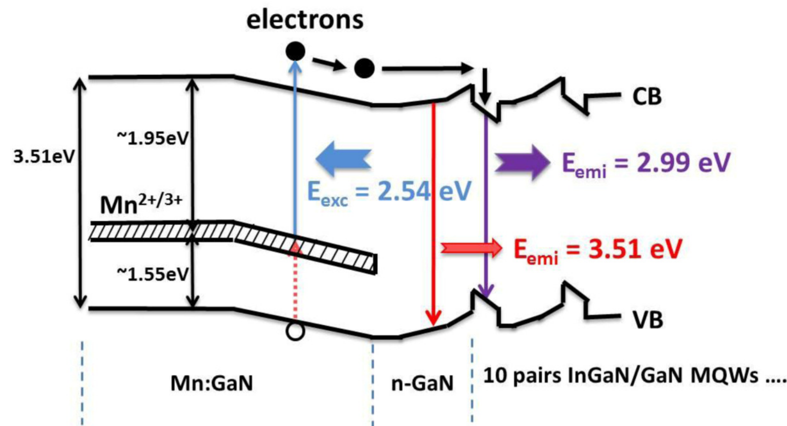

Fig. 6. Schematic band diagram of sample A and the up-converted PL excitation process resulting in emission at 2.99 eV (E_{emi} = 2.99 eV) and 3.51 eV (E_{emi} = 3.51 eV).

Figure 6 shows the schematic band diagram for sample A and the up-converted PL excitation (E_{exc} = 2.54 eV) process resulting in the emission at 2.99 eV (E_{emi} = 2.99 eV). The incident photons (2.54 eV) cannot induce the band-to-band transition. However, they can mediate the electronic transition from the valance band to the Mn impurity band and/or the transition from the Mn impurity band to the conduction band. If a two-photon absorption process occurs, a transition from the valence band through the Mn impurity band to the conduction band should be mediated by the lower-energy photon absorption. In this study, the spectral responses and power dependent UPL measurements indicated that electrons could be excited from the Mn impurity band to the conduction band by the 2.54 eV single-photon absorption process. The electrons were subsequently swept away from the Mn-doped GaN photodetection layer and injected into the InGaN/GaN MQW layers. The injection was

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achieved via the internal electric field at the step doping junction (undoped/Si-doped junction). Part of these electrons eventually fell down the valence bands of InGaN/GaN QWs and the *n*-GaN spacer layer. Consequently, the UPL emission peaks at 2.99 and 3.51 eV appeared, respectively.

In principle, the up-conversion mechanism should be beneficial for energy harvesting. However, the up-conversion quantum efficiency was still low, $\eta \sim 8 \times 10^{-3}\%$. For a practical PV cell including the up-conversion structure, conversion efficiency contributing from the up-conversion mechanism would be far less than that of active layer of PV cell. Therefore, it is difficult to clarify whether this mechanism would be beneficial for energy harvesting or not before the up-conversion quantum efficiency is further boosted.

4. Conclusions

In summary, we have proposed an up-converted heterostructure based on a homologous GaN-based material system. The system involved the stacking of Mn-doped GaN intermediate band materials and InGaN/GaN MQW structures to generate up-converted photo-carriers via the absorption of lower-energy photons. This process led to a higher-energy photon emission via radiative recombination in QWs, respectively. Power-dependent PL and spectral responses indicated that the UPL originated from a single-photon absorption process and photo-carrier injection from the Mn-doped GaN layer to InGaN/GaN MQWs. The proposed scheme could be interpreted within the uncomplicated energy level model, and linearly up-convert photons from 2.54 to 2.99 eV without external bias voltage.

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