Plasmonic Enhancement in InGaN/GaN MQW System with Au Nanoparticles

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Introduction

Currently in optoelectronics GaN based InGaN heterostructure is an important component for production of high efficiency UV, blue and green LEDs and LDs. [1, 2] In order to enhance the commercial viability of InGaN-based components such as white-light LEDs, the overall efficiency of the devices must be increased. [3] Various active and passive techniques for improving the efficiency of InGaN quantum wells are being developed. This includes optimization of epitaxial growth to enhance the radiative recombination process [1-3] or increasing the recombination efficiency of the system via coupling to surface plasmons, as was demonstrated by Okamoto, et al. [4, 5] and Neogi, et al. [6] Unlike conventional III-V semiconductor light emitters based on GaAs or InP, large lattice mismatch in nitride based semiconductors results in strong built-in polarization fields and high defect densities including threading dislocation (TDs) [7-10]. These defects disturb the surface of the thin films or heterostructures and therefore result in a modification of the free carrier and excitonic properties of the nitride semiconductors [9].

Compared to lattice matched semiconductors, InGaN/GaN heterostructures exhibit high internal quantum efficiencies even in the presence of high defect densities. GaN based heterostructures including InGaN/GaN are normally grown along the c-axis. One common defect in InGaN/GaN systems linked to the TDs is the Inverted Hexagonal Pit (IHP) or "V-shaped" Pit. These pits are normally formed during the incorporation of In at relatively lower temperatures (~ 800 ºC) compared to GaN growth temperatures due to small surface perturbations. These perturbations tend to produce (inclined) facets with the lowest growth rate. These are defects caused by strain relaxation during growth centered around a thread defect. Normally these centers should act as non-radiative recombination centers, however it has been known for some time now that these IHPs do not act as such, but instead just reduce the active area of the quantum wells. [1], [2]

The IHPs present an interesting opportunity for the inclusion of metallic nanoparticles for plasmonic coupling. Such particles would essentially sit within the well structure itself allowing for more direct coupling between the nanoparticle's Localized Surface Plasmons (LSPs) and the quantum well structure. This infiltration of metallic nanocrystals into the IHPs presents a means of allowing QW-SP coupling to occur and results in a modification of photonic density of states. [11]

A means for infiltration of nanoparticles into the IHPs was demonstrated by Pereira, et al. previously [11], and here we present preliminary results of PL and Near-field spectroscopy showing an anomalous enhancement due to Au nanocrystals infiltrated into the IHPs.

Experiment/Results

InGaN/GaN multiple quantum wells were grown on Sapphire (001) substrate in a Aixtron 200/4 RF-S horizontal-flow MOCVD reactor. Ammonia, trimethylgallium and tri-methylindium were used as precursors, without the use of any intentional dopant. The GaN buffer layers were grown at 1140ºC in ambient hydrogen-ammonia atmosphere. Typically 1-µm GaN buffer layers were grown to achieve atomically flat terraced structures, and a typical total threading dislocation density of 2-3 x 10^9 cm^{-2}. InGaN/GaN quantum wells with 14 periods were grown at 860 ºC. Details of the growth conditions can be found in Ref. [12]. AFM measurements were performed with a commercial MultiMode scanning probe microscope (Multimode, Nanoscope IIIA, DI). We have used a commercial tip-cantilever SuperSharpSilicon™ system SSS-NCL Nanosensors with a spring constant of k = 48 N/m and typical tip radius of 2 nm, half-cone angle < 10° at the last 200 nm of the tip was used. Surface imaging was performed in the non-contact mode (tapping mode with resonance frequency at 190 kHz) at the scanning speed 1-5 µm/s. Cross-section transmission electron microscopy (TEM) images were obtained on a Philips CM30 TEM operating at 300 keV. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was carried out on a FEI Tecnai F20 FEGTEM using an accelerating voltage of 200 keV. Spatially resolved high resolution near-field photoluminescence of the MWQ sample was measured using a Near-field Scanning Optical Micro-spectrometer (JASCO NFS-330). The sample was illuminated with metal-coated UV fiber probes having a nominal apical aperture of 90-180 nm. The excitation was provided in the near-field limit that enabled local excitation of the IHPs with high spatial limited by the dimension of the probe aperture and high spectral resolution (~ 0.01 nm). A HeCd laser with excitation energy at 325 nm was used for the excitation process. The excitation intensity at the source of the fiber tip was about 5 µW. Far-field Angle and Temperature-Dependent PL were done using a spectrometer/CCD coupled to a optical transfer tube with an iris capable of rotating from -25 to 90 degrees, 0 degrees being normal to the sample. For the Temperature Dependence the probe was left normal to the surface, while varying over the full range for the Angle Dependence.

Figure 1 shows the Near-field Intensity over a 1x1 micron area along with the spectra taken at two distinct points, one representing an enhanced area due to an Au Nanocrystal and the second representing the bare surface. As can be seen from the spectra, the enhanced area has an intensity around 50% brighter than the bare surface (point 2), and around 5-600% brighter than the empty pits (point 3).

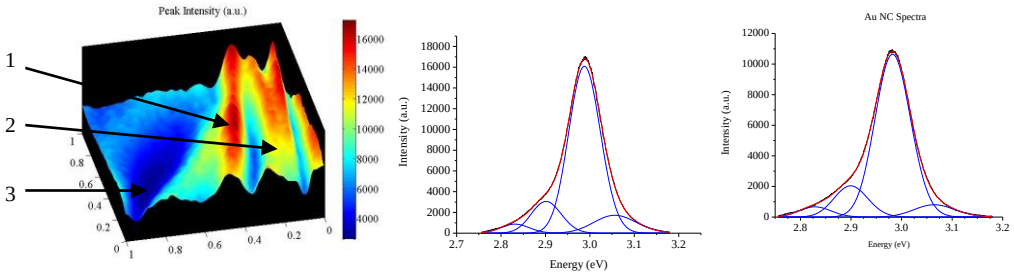

Fig. 1: (a) Near-field Intensity map of a 1x1 micron area showing two peaks due to Au NCs. (b) Fitted spectra from point 1 which corresponds to the enhanced emission from the Au NC. (c) Fitted spectra from point 2 which corresponds to the bare surface.

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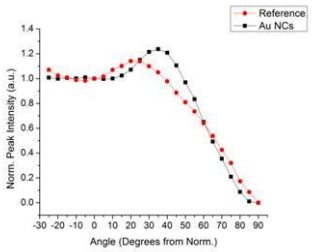

Fig. 2. Angle Dependent PL (Normalized to 1 normal to the surface).

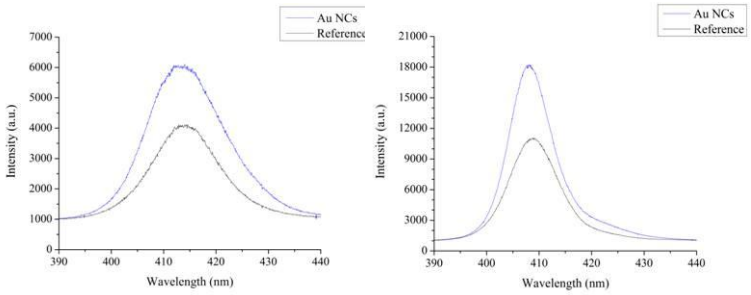

Fig. 3. Photoluminescence measurements of the two samples at 300K (a) and 77K (b)

Figure 2 shows the results of the Angle-Dependent PL measurement at room temperature. It is interesting to note that the Au Nanocrystals show both a shift in the peak emission angle as well an enhancement in the peak emission intensity relative to the normal. The reference sample shows a peak emission at roughly 25 degrees with an intensity of roughly 1.13x the normal. The Au NC sample sees a shift of about 10 degrees and a peak emission of around 1.3x the emission at normal.

Figure 3 shows the Far-Field PL measurements for the Au NC sample and the reference at room temperature and 77K. Here again the enhancement provided by the Au NCs can be clearly seen and it is also shown that the enhancement increases slowly as temperature decreases, going from around 50% enhancement in the far-field at room temperature to around 57% at 77K.

Currently it is conjectured that the enhancement is due to two mechanisms, the first being emission due to scattering of plane-wave modes by the nanoparticles which essentially increases the emission surface area of the sample to include the filled pits. The second is likely to be an interaction between the nanoparticles and the low-energy tail of the emission, which is composed of the first and second phonon replicas of the main peak. While it is not clear from the current data that this enhancement is plasmonic in nature, it is clear that there is an interaction between the Au NCs and the sample producing a significant change in the behavior of the sample.

Conclusions

We have shown clear signs of enhancement due to Au Nanocrystals in an InGaN/GaN MQW system. While direct plasmonic enhancement of the emission should not be possible given the lack of overlap between the Au plasmon resonance and the main emission peak, the evidence suggests that some form of enhancement must be present. While it is not entirely clear that the enhancement is plasmonic in nature, it is clear that further investigation into the interactions of the Au NCs in the InGaN system is warranted. Time-Resolved Photoluminescence Lifetime measurements in particular are an excellent candidate for further investigating the nature of the mechanism generating the enhancement.

References

[1] S. Nakamura, "The roles of Structural Imperfections in InGaN-Based Blue Light-Emitting Diodes and Laser Diodes," *Science, New Series,* Vol. 281, No. 5379, pp. 956-961, Aug 1998.

[2] S. J. Rosner, E. C. Carr, M. J. Ludowise, G. Girolami, and H. I. Erikson, "Correlation of Cathodoluminescence inhomogeneity with microsturctural defects in epitaxial GaN grown by metalorganic chemical-vapor deposition," *Appl. Phys. Lett.* 70 (4), Jan. 1977.

[3] S. Nakamura and G. Fasol, *The Blue Laser Diode: GaN-Based Light Emitting Diode and Lasers,* Berlin: Springer, 1997.

[4] K. Okamoto, I. Niki, A. Shvartser, Y. Narukawa, T. Mukai, and A. Scherer, "Surface-plasmon-enhanced light emitters based on InGaN quantum wells," *Nature Materials,* Vol. 3, 2004.

[5] K. Okamoto, et al., "Surface plasmon enhanced bright light emission from InGaN/GaN," *Phys. Stat. Sol.* (a) 204, No. 6, pp. 2103-2107, 2007.

[6] A. Neogi et al, "Enhancement of spontaneous recombination rate in a quantum well by resonant surface plasmon coupling ", Phys. Rev. B, Vol. 66, 153305 (2002)

[7] H. Morkoc. Nitride Semiconductors and Devices, Berlin : Springer-Verlag, 1999.

[8] A. Neogi, "Near Field Optical Spectroscopy of GaN/AlN Quantum Dots", IEEE Trans. Nanotechnology, Vol. 4, pp. 297-299, Mar. 2005.

[9] A. Hangleiter, F. Hitzel, C. Netzel, D. Fuhrmann, U. Rossow, G. Ade, and P. Hinze, "Suppression of Non-radiative Recombination by V-Shape d Pits in GaInN/GaN Quantum Wells Produces a Large Increase in the Light Emission Efficiency," *Phys. Rev. Lett.* 95, 127402, 2005.

[10] C. Netzel, H. Bremers, L. Hoffmann, D. Fuhrmann, U. Rossow, and A. Hangleiter, "Emission and recombination characteristics of GaInN/GaN quantum well structures with nonradiative recombination suppression by V-shaped pits," *Phys. Rev. B,* 76, 155322, 2007.

[11] S. Pereira, et al., "Controlled Integration of Nanocrystals in Inverted Hexagonal Nano-Pits at the Surface of Light-Emitting Heterostructures," Adv. Mater. 20, pp. 1038-1043, 2008.

[12] Deatcher, C. J., Liu, C., Pereira, S., Lada, M., Cullis, A. G., Sun, Y. J., Brandt, O., Watson, I. M. In situ optical reflectometry applied to growth of indium gallium nitride epilayers and multi-quantum well structures. *Semiconductor Science and Technology* 18 (4): 212-218 (2003).