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Surface-Plasmon-Enhanced Light-Emitting Diodes**

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As the brightness of GaN-based light-emitting diodes (LEDs) has increased, they have recently attracted considerable interest for use in full-color display panels, traffic signals, and solid-state lighting, because of their many advantages, such as long lifetime, small size, and low energy consumption.[1,2] In spite of these advantages, the overall external quantum efficiency, which depends on the internal quantum efficiency (IQE) and the light extraction efficiency (LEE), is still low in conventional $In_xGa_{1-x}N$/GaN quantum well (QW) structures. The IQE is strongly influenced by nonradiative recombination processes, by dislocations and other defects, and by separation of the electron and hole wave functions by spontaneous polarization and strain-induced piezoelectric polarization. The LEE is limited by the total internal reflection of generated light and successive re-absorption due to the high refractive index difference between LED structures and air. Recently, it has been suggested that surface plasmons (SPs), excited on a rough metallic surface by the interaction between light and metal, can significantly enhance light emission by improving the IQE.[3–14] Although it has been shown that SPs can significantly enhance the quantum efficiency of InGaN emitters, the realization of a GaN-based LED structure with QW-SP coupling has not yet been reported. Here, we demonstrate for the first time an SP-enhanced InGaN/GaN multiple quantum well (MQW) blue LED with a Ag nanoparticle layer inserted between the n-GaN layer and the MQW layer.

SPs have attracted great interest because optical properties can be greatly enhanced by coupling between SPs and the QW in LEDs. The coupling of spontaneous emission from the QW into the SP mode can be observed due to the increased absorption at the SP frequency.[10] Time-resolved photoluminescence (TR-PL) measurements showed that the recombination rate in the QW was 90 times faster than spontaneous emission from the QW, when the emission was resonantly coupled to a SP.[11] Recently, Okamoto et al.[12] reported a 14-fold PL enhancement and a 6.8-fold IQE enhancement of InGaN QWs by QW-Ag coupling. Despite the significant enhancement of the IQE of InGaN emitters by SPs, the realization of a GaN-based LED structure with QW-SP coupling is yet to be reported. In previous optical studies[10–12] a metal layer was deposited on the surface of the InGaN QW structure together with a GaN spacer layer of thickness 10∼12 nm for efficient QW-SP coupling, in order to observe the PL enhancement of the QW, because electron–hole pairs located within the near-field of the QW surface can couple to the SP mode. To realize SP-enhanced LEDs, the metal layer should be deposited on a p-type GaN/MQW structure and the thickness of that p-type GaN layer is critical for QW-SP coupling. The penetration depth of the SP fringing field into the semiconductor is given by $Z = \lambda/2\pi[(\varepsilon'_{\mathrm{Gan}} - \varepsilon'_{\mathrm{metal}})/\varepsilon'^{2}_{\mathrm{GaN}}]^{1/2}$, where $\varepsilon'_{\mathrm{GaN}}$ and $\varepsilon'_{\mathrm{metal}}$ make up the real part of the dielectric constant of the semiconductor and metal.[12] The penetration depth Z was estimated to be 42 nm for QW-SP coupling at an emission energy of 2.7 eV (459.2 nm) for a blue LED using the real part of the dielectric of the GaN and Ag metal.[15,16] Therefore, the thickness of the p-GaN layer in the blue LEDs should be less than 42 nm to allow QW-Ag coupling to occur. However, the thickness of the p-GaN layer should be large enough to maintain the p-n junction in LEDs. Here, the depletion width of the p-side in the p-n junction can be estimated to find a minimum thickness for the *p*-GaN layer. The depletion width of the *p*-side can be calculated from

$$x_{p0} = \left(\frac{2\varepsilon V_{bi} N_D}{qN_A(N_A + N_D)}\right)^{\frac{1}{2}} \quad (1)$$

where x_{p0} is the depletion width of the *p*-side, ε is the dielectric constant, N_{D} is the carrier concentration of the n-GaN layer, N_{A} is the carrier concentration of the p-GaN layer, and V_{bi} is the built-in voltage

$$V_{bi} = \frac{kT}{q} \ln \frac{N_A N_D}{n_i^2} \quad (2)$$

where n_{i} is the intrinsic carrier concentration.[16–18] If the carrier concentration of the n-GaN layer and p-GaN is

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$1 \times 10^{18}\,cm^{-3}$ and $1 \times 10^{17}\,cm^{-3}$, respectively, the depletion width of the p-side is estimated to be 76 nm. Therefore, the thickness of the p-GaN layer should be greater than 76 nm for formation of a p-n junction in a blue LED, but such a layer thickness is too large for QW-SP coupling. Here, we propose a SP-enhanced InGaN/GaN QW LED structure with a Ag nanoparticle layer inserted between the *n*-GaN layer and the MQW layer. TR-PL measurements clearly showed that the PL decay time of the LED with a Ag nanoparticle layer was significantly decreased compared to the PL decay time of the LED without a Ag nanoparticle layer, indicating that the spontaneous emission rate was increased by QW-SP coupling. The optical output power of the LED was also significantly increased by QW-SP coupling.

The LEDs were fabricated specifically for this study to verify the improvement of the emission efficiency through QW-SP coupling. Figure 1 shows a schematic 3D representation of a blue LED structure with a Ag nanoparticle layer. The Ag nanoparticle layer was inserted between the n-GaN layer and the MQW layer for coupling between the SP and the QW.

Figure 2 shows atomic force microscopy (AFM) images of Ag nanoparticles deposited on a n-GaN layer a) before and b) after annealing at a temperature of 750 °C for 10 min in a metal–organic chemical vapor deposition (MOCVD) growth chamber, which was at the same temperature for growth of the MQW with blue light emission. The diameter and the height of the Ag nanoparticles before the annealing process were (275 ± 50) nm and (8 ± 4) nm, respectively. After annealing, the diameter and the height of Ag nanoparticles were increased to (450 ± 50) nm and (15 ± 5) nm, respectively. The size of the Ag nanoparticles was increased by thermal annealing via Ostwald ripening of the nanoparticles.[19] Figure 2b shows dark pinholes on the *p*-GaN layer, which can be attributed to threading dislocations. Figure 2b also shows the hole in the Ag nanoparticles. After annealing the number density of the Ag nanoparticles was $6.4 \times 10^{7}\,cm^{-2}$ and the surface area coverage was only 3% of the n-GaN layer area.

To evaluate the interfacial and structural characteristics of the InGaN/GaN MQWs of LEDs with and without a Ag nanoparticle layer, a high resolution X-ray θ-2θ measurement was performed. Figure 3 shows the (0002) reflection obtained with a θ-2θ scan along the growth direction of 5 periods of InGaN/GaN MQWs with and without a Ag nanoparticle layer, respectively. The 0^{th} order peak represents the average indium composition in the pair of InGaN/GaN layers and the high-order peaks represent the thickness of the barrier and the QW layer.[20] Separation of the 0^{th} order peak as well as the other high order peaks toward that of the underlying GaN layer is almost identical in LEDs with and without the Ag nanoparticle layer, respectively. This result indicates that the structure of a MQW having a Ag nanoparticle layer was not degraded compared to the structure of a MQW without a Ag nanoparticle layer.

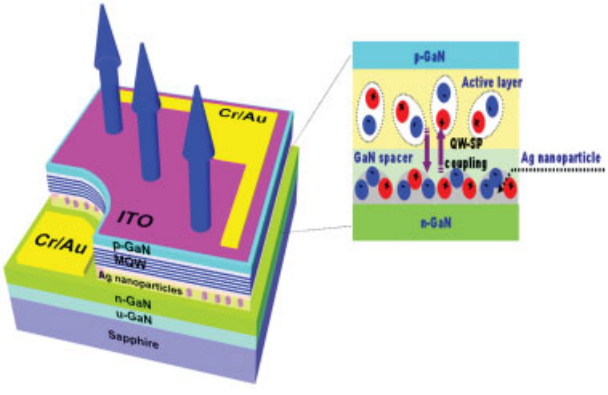

Figure 1. Schematic 3D representation of a InGaN/GaN LED with embedded Ag nanoparticles.

Figure 4 shows the PL spectra of InGaN/GaN MQW LEDs with and without a Ag nanoparticle layer and their wavelength-dependent PL enhancement. The integrated PL intensity of LEDs with a Ag nanoparticle layer is twice as strong as that of LEDs without a Ag nanoparticle layer. To confirm that the observed PL enhancement is not due to reflection of light from the Ag nanoparticles, we measured the transmittance of Ag nanoparticles surrounded by a GaN layer. The sample was prepared by growing a GaN layer on Ag nanoparticles deposited on a GaN substrate. As shown in the inset of Figure 4b, the transmittance of a Ag nanoparticle layer was nearly 99.5%, indicating that the increase of PL intensity was not due to reflection of light by the Ag nanoparticle layer. It should also be noted that the transmission spectrum of the Ag nanoparticles exhibited absorption over a range of 396 to 455 nm, which can be attributed to the extinction of the excitation of dipole plasmon modes in the Ag nanoparticles.[21,22] Figure 4b shows that the PL spectrum of MQWs with a Ag nanoparticle layer is significantly enhanced compared to the PL spectrum of MQWs without a Ag nanoparticle layer, especially at a wavelength of around 453 nm, where the plasmon mode of the Ag nanoparticles can be coupled to the QW, as shown in the inset of Figure 4b. When the exciton dipole energies of the InGaN QW and the SP energy of the metal are similar, the excited dipole energies in the InGaN QW can be transferred into SP modes of the metal.[13,14] The roughness or the nanostructure of the metal layer allows SPs of high momentum to scatter, lose their momentum, and couple to radiated light. This process was much faster than the recombination rate of the exciton dipole in the InGaN QW.[14] Therefore, the increase in the PL intensity of LEDs with Ag nanoparticles can be attributed to QW-SP coupling.

Figure 5 shows TR-PL spectra of InGaN/GaN MQW LEDs with and without a Ag nanoparticle layer measured at room temperature (300 K) and at low temperature (10 K), respectively. The decay curves of the TR-PL showed two kinds of decay rate. The fast decay component results from exciton recombination, while the slow component corresponds to localized carrier recombination by the quantum-confined Stark effect (QCSE). To find the coupling between an exciton of the MQW and the SPs of the Ag nanoparticles, the initial, fast part of each decay curve was fitted with a monoexponential decay

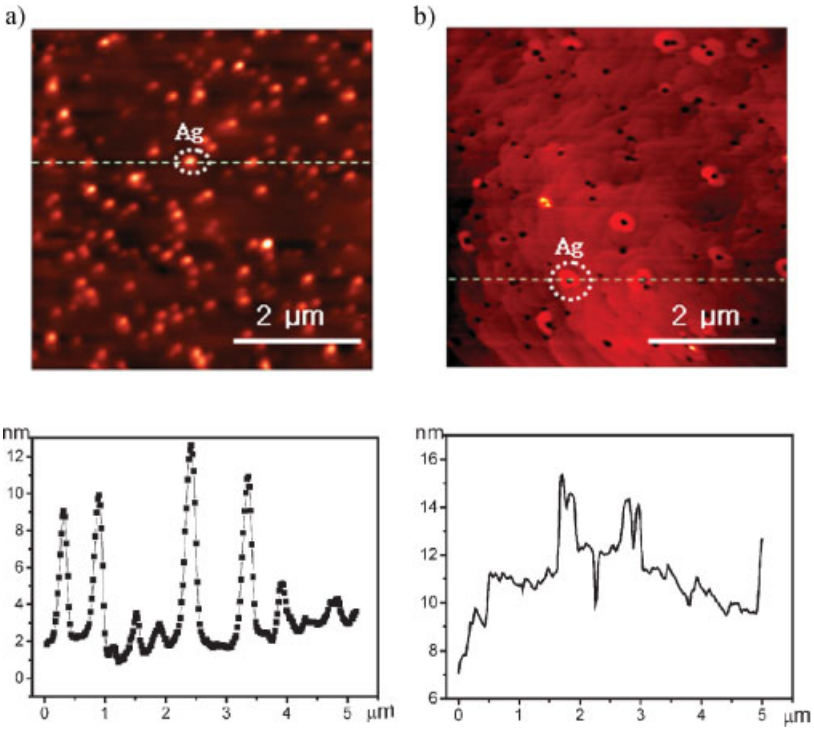

Figure 2. a) Atomic force microscopy (AFM) image of Ag nanoparticles deposited on a n-GaN layer before annealing. b) AFM image of Ag nanoparticles deposited on a n-GaN layer after annealing. The annealing process was carried out at a temperature of 750 °C for 10 min in a metal–organic chemical vapor deposition growth chamber.

model, shown as dashed lines in Figure 5. The curves shows that the effective exciton lifetime of LEDs with a Ag nanoparticle layer decays faster, both at 10 K and 300 K, than that of LEDs without a Ag nanoparticle layer. The effective exciton lifetime of LEDs with a Ag nanoparticle layer was 175 ps at 10 K and 80 ps at 300 K, respectively, while the effective exciton lifetime of LEDs without a Ag nanoparticle layer was 470 ps at 10 K and 140 ps at 300 K, respectively. The faster decay time for LEDs with a Ag nanoparticle layer was attributed to the coupling of the QW with SPs in the Ag nanoparticles. When the exciton energy of the QW is close to the electron vibration energy of the SP at the Ag-GaN surface, exciton energy can transfer to the SP. The PL decay rates are then enhanced through the QW-SP coupling rate, which is expected to be very fast compared to the radiative and nonradiative recombination rates of the QW.[23] A Purcell enhancement factor (F_p) can be calculated to describe this remarkable increase in spontaneous emission rate as $F_p(w) = \tau_{PL}(\omega)/\tau^*_{PL}(\omega) = k_{PL}\ ^*(\omega)/k_{PL}\ (\omega)$, where $k_{PL}\ (\omega)$ and $k_{PL}\ ^*(\omega)$ are the original and enhanced PL decay rate, respectively.[24] In the present study, values for F_p were 1.75 (at 300 K) and 2.68 (at 10 K), respectively, at an emission energy of 2.7 eV (459 nm). The F_p value at 300 K was smaller than the F_p value at 10 K due to the nonradiative recombination process, which competes with the SP. Therefore, the enhanced F_p also indicates that the PL intensity of a MQW LED with a Ag nanoparticle layer, as shown in Figure 4b, can be attributed to an increase in the spontaneous emission rate due to SP-QW coupling.

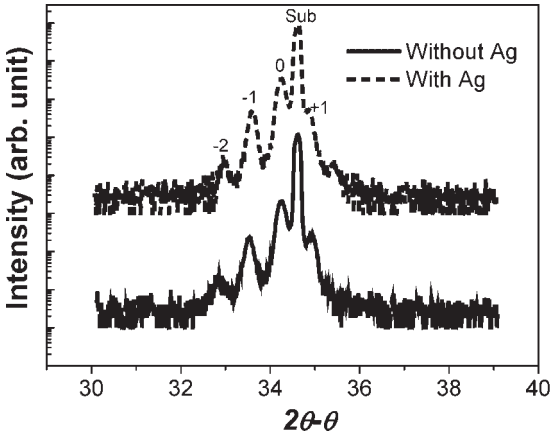

Figure 3. θ-2θ X-ray diffraction scan spectra of InGaN/GaN MQW LEDs with Ag nanoparticles (dashed line) and without Ag nanoparticles (solid line).

The current–voltage (I–V) characteristics and the optical output power of a blue LED with and without a Ag nanoparticle layer are shown in Figure 6. The forward voltages of an LED with and without a Ag nanoparticle layer were 3.90 V and 3.85 V, respectively. These results indicate that inserting a Ag nanoparticle layer into a blue LED has not caused the electrical properties to deteriorate. The optical output power of an LED with a Ag nanoparticle layer was 32.2% higher than the optical output power of an LED without a Ag nanoparticle layer at an input current of 100 mA. The improvement in optical output power can be attributed to an increase in the spontaneous emission rate by resonance between excitons in the QW layer and the SPs in the Ag nanoparticles. A large enhancement of the F_p and output power of the LED is expected if the size and density of Ag nanoparticles are further optimized,[21,22,25] suggesting that the SP-QW coupling by embedded Ag nanoparticles is a very promising way to develop high-efficiency LEDs as a solid-state lighting source.

In conclusion, in this paper we present SP-enhanced InGaN/GaN MQW blue LEDs containing embedded Ag nanoparticle layers. The optical output power of these LEDs was enhanced by 32.2% at an input current of 100 mA. TR-PL results showed that the PL decay time of LEDs containing Ag nanoparticles was significantly decreased compared to the PL decay time of LEDs without Ag nanoparticles, indicating that the spontaneous emission rate was increased by energy transfer between

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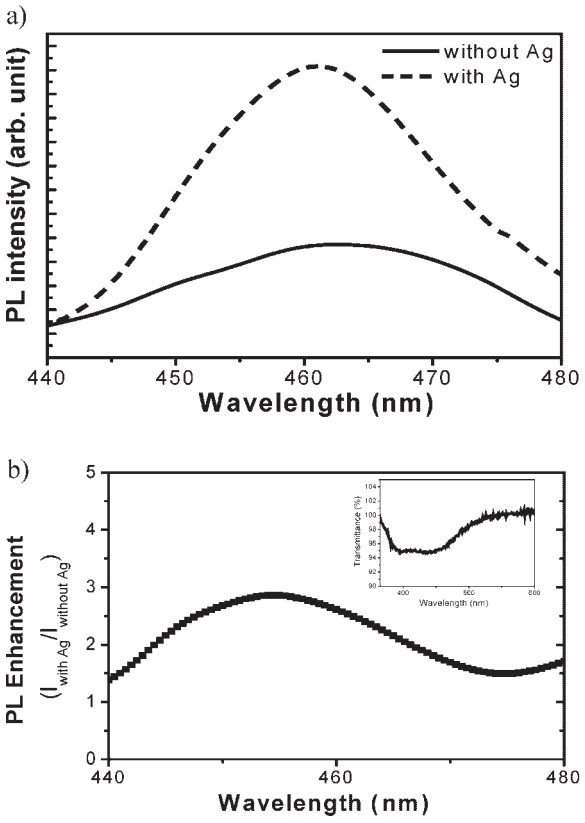

Figure 4. a) Photoluminescence (PL) spectra of a InGaN/GaN MQW LED with Ag nanoparticles (dashed line) and without Ag nanoparticles (solid line) at 300 K. b) PL intensity enhancement (ratio of the two PL curves shown in (a). The inset shows the transmittance spectrum of Ag nanoparticles.

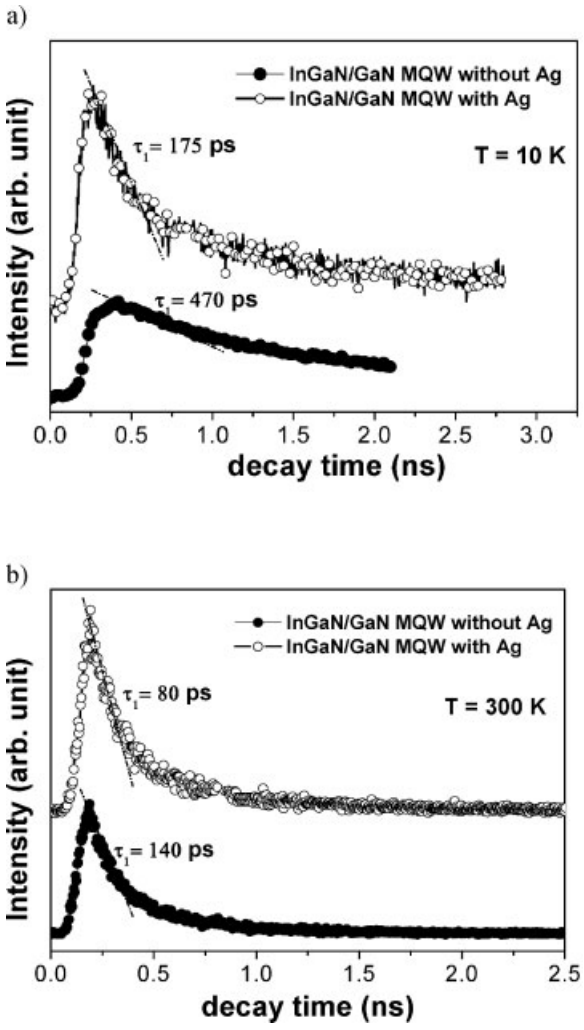

Figure 5. a) Time-resolved PL spectra of InGaN/GaN MQW LEDs with Ag nanoparticles (white-dotted line) and without Ag nanoparticles (black-dotted line) at T = 10 K. b) Time-resolved PL spectra of InGaN/GaN MQW LEDs with Ag nanoparticles (white-dotted line) and without Ag nanoparticles (black-dotted line) at T = 300 K.

the QW light emitter and the SPs of the Ag nanoparticles. These findings show that Ag nanoparticles can be used effectively to greatly increase the IQE of InGaN/GaN blue LEDs due to the strong coupling of QWs with SPs from the Ag nanoparticles.

Experimental

LED Fabrication: The blue LED was deposited on a (0001) sapphire substrate by using a growth chamber in a low-pressure metal–organic chemical vapor deposition (LP-MOCVD) system. The substrate was initially treated with H_2 at a temperature of 1050 °C. Subsequently, a 25 nm thick, low-temperature GaN buffer layer was grown at 550 °C. After high-temperature annealing of the buffer layer, a 2 μm thick undoped GaN layer and a 2 μm-thick n-type GaN layer were grown at 1040 °C. Then, the samples were removed from the growth chamber in order to deposit a Ag nanoparticle layer. Ag nanoparticles of 5∼8 nm were deposited on the n-GaN layer by electron-beam (e-beam) evaporation. After deposition of a Ag nanoparticle layer, the samples were reloaded in the growth chamber. A 20 nm thick undoped GaN layer was then grown on the Ag nanoparticle layer as a capping layer. A InGaN/GaN MQW, which consisted of 5 periods of 2 nm thick $In_{0.2}Ga_{0.8}N$ wells and 12 nm-thick GaN barriers, was subsequently grown at a temperature of 750 °C. Finally, a 0.2 μm-thick p-type GaN layer was deposited on the MQW at a temperature of 950 °C. The fabrication of the LED was accomplished as follows: the surface region of the p-GaN layer was partially etched by an inductively coupled plasma-etching process using $CH_4/Cl_2/H_2$/Ar gases to expose the n-GaN layer. Then, an indium tin oxide (ITO) layer with a thickness of 200 nm was deposited as a transparent, current-spreading layer on the p-GaN layer. This was followed by the deposition of Cr/Au(20/100nm) on the n-GaN layer as an n-pad electrode and on the transparent, current-spreading layer as a p-pad electrode by e-beam evaporation.

Measurements: The electrical and optical properties of the LEDs were measured using a parameter analyzer (HP-4155A) and a calibrated Si-photodiode connected to an optical power meter, respectively. PL measurements were carried out using a He–Cd laser operating at a wavelength of 325 nm. To perform time-resolved PL measurements, the frequency-doubled output from a mode-locked femtosecond laser was used. The values for the pulse width, wavelength, and repetition rate were chosen as 200 fs, 350 nm, and 76 MHz, respectively. A Hamamatsu Photonics microchannel plate-photomultiplier tube (R3809U-59) was used as detector. The temperature dependence of

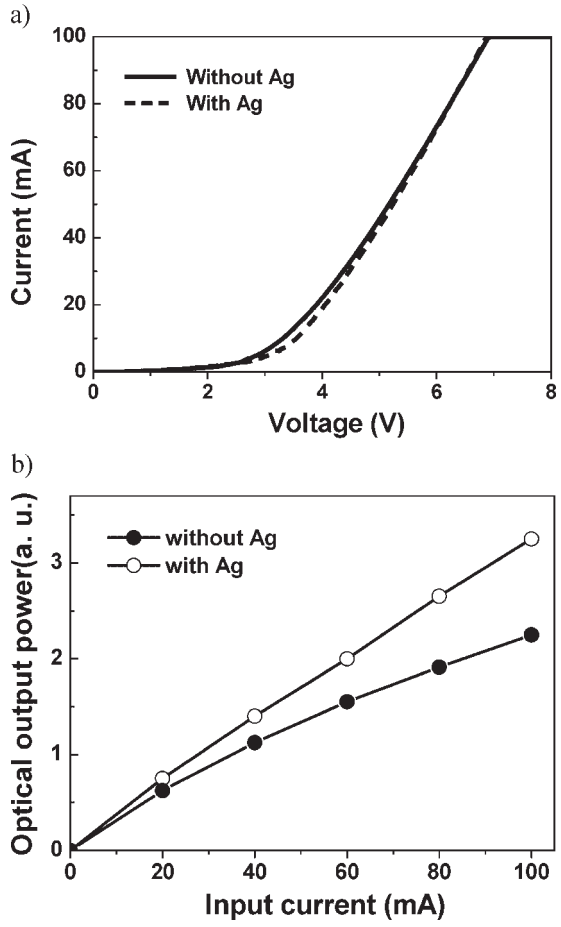

Figure 6. a) *I–V* characteristic of InGaN/GaN MQW LEDs with Ag nanoparticles (dashed line) and without Ag nanoparticles (solid line). b) Optical output power (*L–I* characteristic) of InGaN/GaN MQW LEDs with Ag nanoparticles (white-dotted line) and without Ag nanoparticles (black-dotted line).

the photoluminescence process was studied within a cryostat capable of cooling from room temperature down to about 10 K.

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[1] R. M. Fletcher, *Opt. Photonics News* **1999**, *10*, 19.
[2] E. F. Schubert, J. K. Kim, *Science* **2005**, *308*, 1274.
[3] A. Köck, E. Gornik, M. Hauser, W. Beinstingl, *Appl. Phys. Lett.* **1990**, *57*, 2327.
[4] N. E. Hecker, R. A. Hopfel, N. Sawaki, *Phys. E* **1998**, *2*, 98.
[5] N. E. Hecker, R. A. Hopfel, N. Sawaki, T. Maier, G. Strasser, *Appl. Phys. Lett.* **1999**, *75*, 1577.
[6] W. L. Barnes, *J. Light. Technol.* **1999**, *17*, 2170.
[7] S. Gianordoli, R. Hainberger, A. Köck, N. Finger, E. Gornik, C. Hanke, L. Korte, *Appl. Phys. Lett.* **2000**, *77*, 2295.
[8] J. Vuckovic, M. Loncar, A. Scherer, *IEEE J. Quantum Electron.* **2000**, *36*, 1131.
[9] P. A. Hobson, S. Wedge, J. A. E. Wasey, I. Sage, W. L. Barnes, *Adv. Mater.* **2002**, *14*, 1393.
[10] I. Gontijo, M. Boroditsky, E. Yablonovitch, S. Keller, U. K. Mishra, S. P. DenBaars, *Phys. Rev. B* **1999**, *60*, 11564.
[11] A. Neogi, C. Lee, H. O. Everitt, T. Kuroda, A. Tackeuchi, E. Yablonovitch, *Phys. Rev. B* **2002**, *66*, 153305.
[12] K. Okamoto, I. Niki, A. Shvartser, Y. Narukawa, T. Mukai, A. Scherer, *Nat. Mater.* **2004**, *3*, 601.
[13] K. Okamoto, I. Niki, A. Scherer, Y. Narukawa, T. Mukai, Y. Kawakami, *Appl. Phys. Lett.* **2005**, *87*, 071102.
[14] W. Barnes, *Nat. Mater.* **2004**, *3*, 588.
[15] E. D. Palik, *Handbook of Optical Constants of Solids*, Vol. 1, Academic, San Diego **1985**, *Part 2.*
[16] S. Adachi, *Handbook of Physical Properties of Semiconductors*, Vol. 2, Kluwer Academic Publishers, New York **2004**, *Ch. 10.*
[17] K. Kano, *Semiconductor Devices*, Vol. 1, Prentice-Hall International, Inc., Upper Saddle River (NJ) **1998**, *Ch. 5.*
[18] V. Bougrov, M. E. Levinshtein, S. L. Rumyantsev, A. Zubrilov, *Properties of Advanced Semiconductor Materials GaN, AlN, InN, BN, SiC, SiGe*, (Eds: M. E. Levinshtein, S. L. Rumyantsev, M. S. Shur), Vol. 1, John Wiley & Sons, Inc., New York, USA **2001**, *Ch. 1.*
[19] P. Sharma, C. Y. Liu, C. Hsu, N. W. Liu, Y. L. Wang, *Appl. Phys. Lett.* **2006**, *89*, 163110.
[20] S. Nakamura, T. Mukai, M. Senoh, S. Nagahama, N. Iwasa, *J. Appl. Phys.* **1993**, *74*, 3911.
[21] H. Mertens, J. Verhoeven, A. Polman, *Appl. Phys. Lett.* **2004**, *85*, 1317.
[22] J. S. Biteen, N. S. Lewis, H. A. Atwater, H. Mertens, A. Polman, *Appl. Phys. Lett.* **2006**, *88*, 131109.
[23] C. K. Choi, Y. H. Kwon, B. D. Little, G. H. Gainer, J. J. Song, Y. C. Chang, S. Keller, U. K. Mishra, S. P. Denbaars, *Phys. Rev. B* **2001**, *64*, 245339.
[24] E. M. Purcell, *Phys. Rev.* **1946**, *69*, 681.
[25] C. Y. Chen, D. M. Yeh, Y. Lu, C. C. Yang, *Appl. Phys. Lett.* **2006**, *89*, 203113.

