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Localized surface plasmon enhanced light-emitting devices

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In this paper, localized surface plasmon enhanced *n*-ZnO/*i*-ZnO/MgO/*p*-GaN structured light-emitting devices have been designed and constructed. It is found that the electroluminescence of the devices can be enhanced at selective wavelengths that match the localized surface plasmon extinction spectra of the metal nanoparticles.

Surface plasmons (SPs) are collective charge oscillations that occur at the interface between a metal and a dielectric.^{1–3} In particular, the collective oscillations of electrons in noble metal nanoparticles (NPs) are localized surface plasmons (LSPs). The resonant excitation of LSPs can lead to selective photon absorption and enhancement of local electromagnetic fields near the metal NPs by several orders of magnitude.^{4–6} Recently, LSPs have been actively employed to enhance the emission of light-emitting materials and devices.^{7–19} There have been quite a few reports on LSPs enhanced photoluminescence (PL) of semiconductors.^{7–11} Okamoto *et al.* reported a 14-fold PL enhancement of InGaN/GaN quantum well by using silver (Ag) layers.⁷ Lai *et al.* and Liu *et al.* showed 15- and 12-fold PL enhancement from ZnO films by using Ag or platinum cap layers.^{9,10} It is accepted that for practical applications, electroluminescence (EL) is necessary in many cases. Therefore, it will be of greater significance and importance if EL can be enhanced by LSPs. In the past few years, several reports have demonstrated LSPs enhanced InGaN/GaN quantum well, Si quantum dots, and *n*-ZnO/*p*-GaN heterojunction light-emitting devices (LEDs).^{12–19} However, compared with the significant PL enhancements, the improvements of EL by LSPs are very tiny. Additionally, it is accepted that the incorporation of metal NPs may alter the carrier transportation in the light-emitting structure, which may also lead to the variation in EL emission. The reduced lifetime of the emission has been regarded as one of the proofs for the LSPs enhanced PL emissions, while the determination of the lifetime of the LSPs enhanced EL emission is much more difficult. The above facts press for more evidence

for LSPs enhanced EL. Nevertheless no such report is available to date.

In this paper, *n*-ZnO/*i*-ZnO/MgO/*p*-GaN light-emitting structures whose emission covers a wide spectrum range have been designed and constructed, and by incorporating metal NPs with different LSP resonance extinction wavelengths into the structure, it is found that the EL of the structure can be enhanced at selective wavelengths that match the extinction spectrum of the metal NPs. The result confirms that the enhancement of the EL in the LEDs is caused by the LSP of the metal NPs.

To construct the LSPs enhanced LEDs, *n*-ZnO/*i*-ZnO/MgO/*p*-GaN structures with a MgO/metal NPs/MgO sandwiched structure inserted between the *n*-ZnO and *i*-ZnO layers have been constructed. The ZnO and MgO films were deposited onto commercially available *p*-GaN/sapphire (0001) templates using a VG V80H plasma-assisted molecular-beam epitaxy (MBE) system. The thickness of the *p*-GaN layer is around 2 μm. Prior to the growths of ZnO and MgO, the *p*-GaN/sapphire templates were pretreated at 600 °C for 30 min to remove any possibly adsorbed contaminants and produce a clean surface. High-purity (6N) elemental zinc and magnesium were used as precursors for the ZnO and MgO growths, and the oxygen source used was radical O produced by cracking oxygen gas in a plasma cell working at 300 W. The pressure during the growth process was fixed at 2×10^{-3} Pa. Firstly, a 20 nm MgO layer, a 50 nm *i*-ZnO layer, and a 10 nm MgO layer were deposited onto the *p*-GaN layer in sequence at 650 °C. For the incorporation of metal NPs into the structures, the samples were removed from the MBE chamber, and cut into four pieces with equal sizes. One piece remains untouched as a reference device. Colloidal silver (Ag) NPs were spin-coated onto the second sample (referred to as Ag-NPs-1), note that the colloidal Ag NPs were prepared by chemical reduction of silver nitrate in aqueous solution with sodium borohydride in the presence of sodium citrate as a stabilizer.²⁰ Another kind of Ag NPs with a different extinction spectrum were deposited onto the third sample using a vacuum evaporation method, and then an annealing at 500 °C was conducted for two minutes to form Ag NPs (referred to as Ag-NPs-2). For the fourth sample, gold (Au) NPs were deposited onto the sample using the vacuum evaporation method, and then an annealing at 700 °C was conducted for two minutes to form Au NPs (referred to as Au-NPs). Then these four samples were reloaded into the MBE chamber, another 10 nm MgO layer and a 220 nm *n*-ZnO layer were grown in sequence onto these samples at 600 °C. Finally, bilayer Ni/Au and

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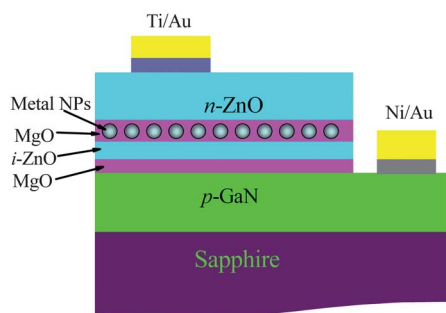


Fig. 1 Schematic diagram of the LSPs enhanced n -ZnO/ i -ZnO/MgO/ p -GaN structure.

Ti/Au electrodes were deposited onto the p -GaN and n -ZnO layer by vacuum evaporation.

The morphology of the NPs was characterized by a Hitachi S4800 scanning electron microscope (SEM). The optical absorption and transmittance spectra were recorded in a Shimadzu UV-3101PC spectrometer. EL measurements of the light-emitting structures were carried out in a Hitachi F4500 spectrometer, and a continuous-current power source was used to excite the structure. Note that all the measurements were performed at room temperature.

Fig. 1 shows the schematic diagram of the LSPs enhanced n -ZnO/ i -ZnO/MgO/ p -GaN structure. The p -GaN layer with a hole concentration and mobility of $5.0 \times 10^{17} \text{ cm}^{-3}$ and $22.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is used as the hole-injection layer, and the n -ZnO layer with an electron concentration of $5.0 \times 10^{18} \text{ cm}^{-3}$ and a mobility of $16.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is acted as a current-distribution layer for the structures. The effect of the MgO layer underneath the i -ZnO layer is to confine electrons into the i -ZnO layer, which has been elucidated in our previous publication.^{21–23} The effect of the two MgO layers outside the metal NPs is to reduce the ohmic loss of the metal NPs.^{24,25} Three kinds of metal NPs

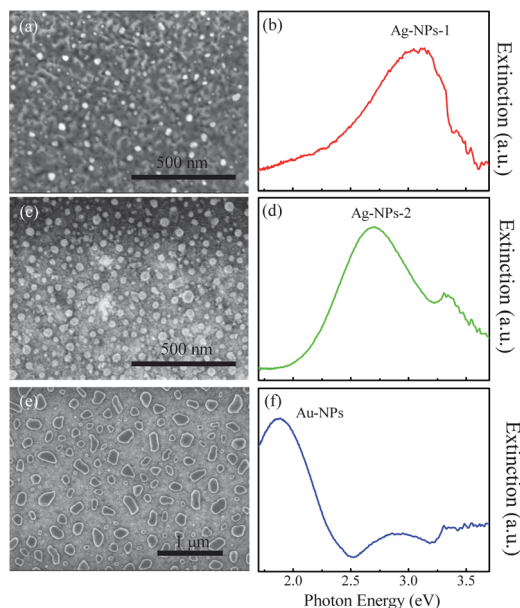


Fig. 2 SEM images of the Ag-NPs-1 (a), Ag-NPs-2 (c) and Au-NPs (e) and the extinction spectra of the Ag-NPs-1 (b), Ag-NPs-2 (d), and Au-NPs (f).

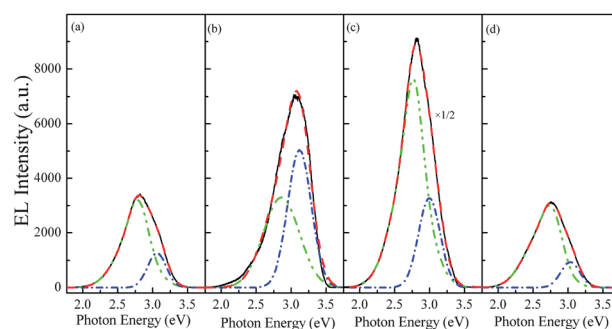


Fig. 3 Room temperature EL spectra of the reference device (a), Ag-NPs-1 (b), Ag-NPs-2 (c), and Au-NPs (d) modified devices at the input power of 130 mW. Note that the dashed lines are fitting results of the experimental data using Gaussian function.

with different LSP resonance extinction wavelengths were employed as the source of LSPs for the structures.

Fig. 2(a) and (b) show the top-view SEM image and extinction spectrum of the Ag-NPs-1. It can be found that the Ag-NPs-1 with a diameter of 10–20 nm are dispersed onto the film randomly, as indicated by the white spots in the image. As shown in Fig. 2(b), the extinction spectrum of the Ag-NPs-1 exhibits a resonance extinction band at around 3.1 eV, which results from the extinction by the excitation of dipole plasmon modes in the Ag NPs. The SEM image and the extinction spectrum of the Ag-NPs-2 are shown in Fig. 2(c) and (d), respectively. It is found that the Ag-NPs-2 with a diameter of 10–40 nm is randomly distributed on the sample surface. For the Ag-NPs-2, two extinction bands were observed, as shown in Fig. 2(d). The band centered at 2.8 eV comes from the dipole oscillation parallel to the substrate plane (in-plane mode), and the shoulder band near 3.3 eV is due to the oscillation of the normal mode (out-of-plane mode).²⁶ The SEM image and the extinction spectrum of the Au-NPs are shown in Fig. 2(e) and (f), respectively. It can be found that island-shaped Au-NPs with the size of 50–300 nm are visible on the sample surface. The extinction spectrum of the Au-NPs exhibits a band at 1.9 eV, as shown in Fig. 2(f), which comes from the collective dipole plasmon resonance of the Au NPs.

Fig. 3(a)–(d) show the EL spectra of the reference device and LSP enhanced devices at an input power of 130 mW. As shown in Fig. 3(a), the EL spectrum of the reference device shows a broad band centered at 2.8 eV and a shoulder at 3.1 eV. According to their position, the former can be attributed to the transition between the electrons in the conduction band to the acceptor levels in the p -GaN, while the latter to the neutral donor bound exciton emission of the i -ZnO layer.^{21–23} For the Ag-NPs-1 modified device, the emission at 3.1 eV has been enhanced greatly, while the one at 2.8 eV remains almost unchanged, as shown in Fig. 3(b). For the Ag-NPs-2 modified device, the 2.8 eV emission band dominates the spectrum. The emission intensity of the Au-NPs modified device changes little compared with the reference

Table 1 The integrated intensities of the EL spectra for the reference device, Ag-NPs-1, Ag-NPs-2 and Au-NPs modified devices

	Reference device	Ag-NPs-1 modified device	Ag-NPs-2 modified device	Au-NPs modified device
Emission at 3.1 eV	422	2132	2498	317
Emission at 2.8 eV	1620	2123	7678	1640

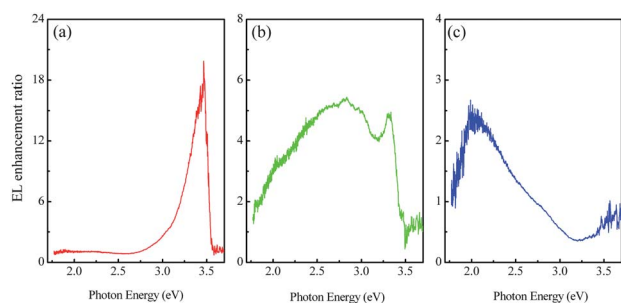


Fig. 4 EL enhancement ratio of the Ag-NPs-1 (a), Ag-NPs-2 (b) and Au-NPs (c) modified devices, which were obtained *via* dividing the emission intensities of the modified devices by that of the reference device.

device. Table 1 shows the variation of the emissions at 3.1 eV and 2.8 eV for the three kinds of metal NPs modified samples. One can see that the integrated intensity of the 3.1 eV emission of the Ag-NPs-1 modified LED is about 4.0-times higher than that of the reference device, while that of the 2.8 eV emission band changes little. For Ag-NPs-2 modified devices, the integrated intensity of the 3.1 eV and 2.8 eV emissions is 4.9 and 3.7 times higher than that of the reference device, respectively. For the Au-NPs modified device, the intensity of the 3.1 eV emission decreases slightly, while that of the 2.8 eV emission band changes little.

To understand the EL enhancement characteristics of the LSPs modified LEDs better, the EL enhancement ratio obtained *via* dividing the emission intensities of the modified devices by that of the reference device is shown in Fig. 4. It is exhibited that the EL enhancement ratio spectra of the LSP enhanced devices are very similar to the extinction spectra of the metal NPs shown in Fig. 2(b), (d) and (f). The above facts indicate undoubtedly that the enhancement comes from the LSPs resonance coupling effect. It is accepted that the EL enhancement of LEDs by LSPs can be contributed by two factors.^{27,28} One is to enhance the internal quantum efficiency of the device by coupling with the carriers in the devices to reduce the capture possibility of the carriers by nonradiative centers. The other is to enhance the external quantum efficiency of the devices by coupling with the photons emitted from the devices to reduce the loss caused by total reflection. Note that the former factor dominates the enhancement when the metal NPs are close to the active layer of the devices, while the latter works mainly when the NPs are deposited onto the surface of the devices. In our *n*-ZnO/*i*-ZnO/MgO/*p*-GaN structure, the metal NPs are embedded 10 nm above the *i*-ZnO active layer. Therefore, we think that the EL enhancement in our case is mainly caused by the resonance coupling effect between the excitons in the *i*-ZnO layer and the LSPs of the metal NPs. The detailed mechanism for the metal NPs surface plasmon enhanced emissions in our case can be understood as follows: in the *n*-ZnO/*i*-ZnO/MgO/*p*-GaN structure, electron-hole pairs are injected into the active layer by the external circuit. For the reference device, these electron-hole pairs may be diminished by radiative or nonradiative recombination, and the emission efficiency is determined by the ratio of these two processes. For the Ag-NPs-1 modified device, the carriers injected into the *i*-ZnO layer with their energy close to 3.1 eV can transfer to the LSP modes of Ag-NPs-1 through the resonance coupling effect since the LSP resonance energy of the Ag-NPs-1 is at around 3.1 eV (as shown in Fig. 2(b)). The generated LSP modes can be extracted as photons. Because the LSP coupling rate is much faster than the

recombination rate of the electron-hole pairs, the electron-hole pairs have a less probability to be captured by nonradiative centers.^{7,8,19} Consequently, the emission at around 3.1 eV can be enhanced. For the Ag-NPs-2 modified device, both the 3.1 eV emission coming from the *i*-ZnO layer and the 2.8 eV emission coming from the *p*-GaN layer can be coupled with the LSP of the Ag NPs because the LSP resonance extinction spectrum of the Ag-NPs-2 overlaps both emission bands (as shown in Fig. 2(d)). Therefore, the emission efficiency of both the 3.1 eV and 2.8 eV bands can be enhanced significantly. For the Au-NPs modified device, the LSP resonance extinction spectrum of the Au-NPs (1.9 eV) overlaps little with the EL spectrum of the *n*-ZnO/*i*-ZnO/MgO/*p*-GaN structure. Then both the emissions at 3.1 eV and 2.8 eV have not been enhanced. The above results show that the EL of the LEDs can be enhanced at selective wavelengths that match the extinction spectrum of the metals. The selective enhancement of EL emissions consolidates that the enhancement in EL emission comes from the resonant coupling effect between the LSPs of the metal NPs and electron-hole pairs in the active layer of the *n*-ZnO/*i*-ZnO/MgO/*p*-GaN structure.

In summary, LSPs enhanced *n*-ZnO/*i*-ZnO/MgO/*p*-GaN structures have been demonstrated. It is found that the EL of the LEDs can be enhanced at selective wavelengths that match the extinction spectrum of the metal NPs. The selective enhancement of EL emission reveals that the enhancement derives from the resonant coupling effect between the LSPs of metal NPs and the carriers in the active layer of the devices.

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