Giant enhancement of top emission from ZnO thin film by nanopatterned Pt

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The authors report the enhancement of the bandgap emission from ZnO thin films by surface modification and surface plasmon cross-coupling. 12-fold and twofold enhancements of bandgap emission from the metal side of ZnO film were observed by sputtering Pt nanopattern and Pt film onto ZnO film, respectively. Time-resolved photoluminescence indicates that the decay time is slowed down by Pt capping, contrary to common observations. The "abnormal" phenomena are interpreted by considering both the surface modification and surface plasmon coupling. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3116617]

Surface plasmon (SP) mediated emission has been proven as an effective means to improve the quantum efficiency of light emitting materials and devices, and a number of experimental results have been reported with various metal structures.[1–10] Wurtzite ZnO, with wide direct bandgap (3.36 eV) and high exciton binding energy (60 meV), is recognized as one of the most promising material for ultraviolet light-emitting devices and laser diodes. Recently, numerous studies have been conducted to improve the band edge emission in ZnO and different metals (Ag, Au, Al, Pt, etc.) have been used as capping layers.[2–9] However, most of the emission enhancements reported so far are in the backward direction in which light is emitted through the substrate into the free space.[6–9] This backward geometry restricts the emitting material to be prepared on transparent substrates. Therefore, the investigation on the enhanced emission from the metal side is very useful and necessary for practical application. To this end, Lei and Ong[5] and Cheng *et al.*[2] have shown two- and threefold band edge emission enhancements from ZnO films by using Al and Ag cap layers, respectively. It was found that the intensity of emission from the metal side is much lower than that of the backward emission due to the strong intrinsic optical absorption of metal. SP mediated emission enhancement has a strong dependence on the morphology of metal films because the coupled SP energy can be only converted to free space radiation via scattering, which bridges the momentum gap; otherwise it should be dissipated, leading to quenching of the emission.[10]

In this letter, we present the remarkably enhanced bandgap emission from Pt nanopattern (NP) capped ZnO. It was found that Pt NP capped ZnO can further enhance the bandgap emission to 12 fold compared to the twofold enhancement observed from flat Pt film capped ZnO. The time-resolved photoluminescence (TRPL) spectra indicated that the PL decay rate of metal capped ZnO is even slower than that of bare ZnO. This result is much different from the reports of other groups[10,11] and we give a detailed interpretation about the mechanism of this abnormal phenomenon.

ZnO films (∼1 μm thick) were deposited on *c*-face sapphire substrates by metal organic chemical vapor deposition,[12] and then were subsequently capped with Pt NP (schematically shown in Fig. 1). A monolayer of highly ordered polystyrene (PS) spheres (500 nm in diameter) was self-assembled on water surface, using a technique reported by Rybczynski *et al.*[13] Such monolayer was then lifted off from the water surface using the aforementioned ZnO/sapphire. Then, Pt was subsequently infiltrated into the monolayer PS/ZnO/sapphire template by a sputtering system. After sputtering, the PS spheres were carefully removed by chloroform dissolving for 30 s in an ultrasonic bath. In order to investigate the influence of Pt NP on the PL spectra of ZnO, a flat Pt film was sputtered onto ZnO as the control sample and the thickness of Pt film (∼30 nm) is the same as the maximum height of Pt NP. All the metal sputtering were carried out at room temperature and no thermal treatment is involved during and after metallization.
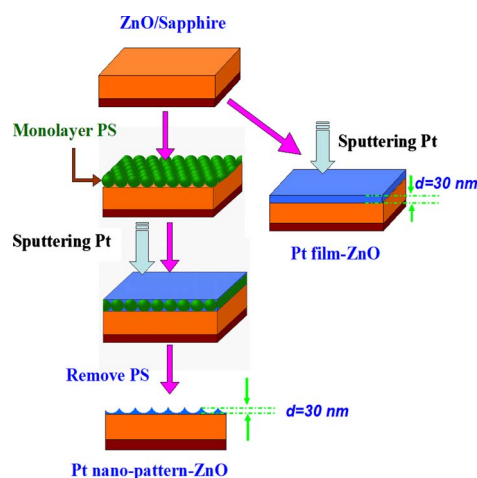

FIG. 1. (Color online) The schematic fabrication process of Pt nanopattern and flat Pt film on ZnO.

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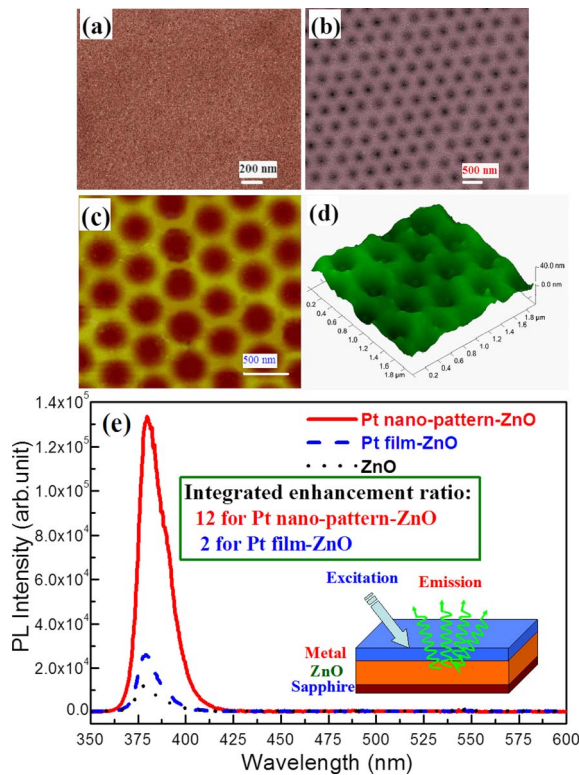
FIG. 2. (Color online) SEM images of (a) the surface of Pt-film/ZnO and (b) Pt nanopattern/ZnO. (c) and (d) are the AFM images of Pt nanopattern/ZnO. (e) is the room temperature PL spectra for Pt nanopattern/ZnO (red solid line), flat Pt film/ZnO (blue dashed line), and bare ZnO (black dotted line). The inset of (e) is the excitation and PL collection configuration.

The morphology of flat Pt film/ZnO and Pt NP/ZnO was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The PL spectra were performed by excitation from a 325 nm line of a He–Cd laser. For TRPL measurements, the sample was excited from the metal side by 340 nm laser pulses generated from an optical parametric amplifier that is pumped using a 100 fs, 1 kHz chirped-pulse amplifier. The TRPL data were collected by an Optronis™ Optoscope streak camera combined with a high-resolution charge-coupled device camera. The overall time resolution of the system is ~50 ps.

Figures 2(a) and 2(b) show the top view SEM images of flat Pt film/ZnO and Pt NP/ZnO, respectively. It can be seen that the surface of Pt film/ZnO is very smooth and continuous and the grain size of Pt film is very small. In Fig. 2(b), highly ordered Pt NP can be clearly observed. In order to further confirm the structure and morphology of Pt NP, we have carried out AFM on Pt NP/ZnO and it is found that the height of the bowls from bottom to top is around 30 nm [presented in Figs. 2(c) and 2(d)].

Figure 2(e) shows the room temperature PL spectra of three samples. The inset is the schematic arrangement of the PL measurement configuration. All samples show strong band edge emission around 380 nm and no obvious defect emission was observed. It is found that the integrated PL intensity of ZnO coated with 30 nm Pt film was two times as strong as that of bare ZnO. This value is comparable with that of previous reports.[2,5] The enhancement by Pt film capping is generally attributed to the interaction between the spontaneous recombination in ZnO and SPs arising from Pt interfaces. Meanwhile, the surface modification (SM) by Pt film may be accounted for this enhancement, as will be ex-
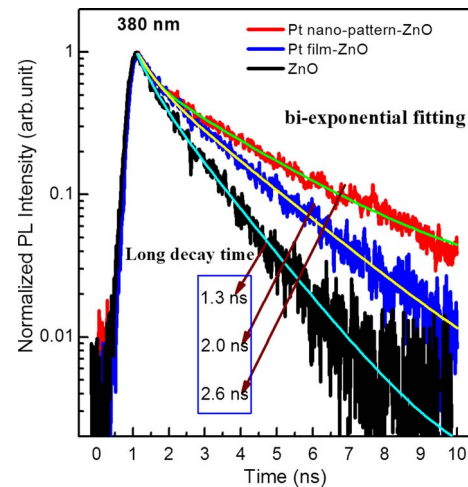

FIG. 3. (Color online) The room temperature TRPL decays of Pt nanopattern/ZnO (red line), flat Pt film/ZnO (blue line), and bare ZnO (black line) at 380 nm.

plained later. For Pt NP/ZnO, the integrated PL intensity is further enhanced by as much as 12 folds, which is remarkably larger than that of previous reports.

Figure 3 shows the room temperature TRPL decays of three samples. All PL decays are fitted using a biexponential function. The instrument temporal response has been deconvolved from the fits. The biexponential decay may be related to the complex dynamics in the ZnO films, which is further complicated by the coexistence of bound and free excitons and their interactions. Further work is in progress to understand the origins of these two lifetimes. The short lifetime component is ~0.3 ns from all three samples and is insensitive to the capping conditions. As the long lifetime component is capping dependent and it determines the overall decay rate, we shall focus on this component in our discussion. It can be seen that the bare ZnO has the fastest decay process with the long decay time constant of 1.3 ns. For Pt NP/ZnO and flat Pt film/ZnO, the long PL decay time constants are 2.0 ns and 2.6 ns, respectively. These observations are contrary to that reported by other groups.[10,11] In these earlier reports, it has been demonstrated that the PL decay rates were increased by the electron-hole pair or exciton-SP coupling rates ($1/\tau_{SP}$), as $1/\tau_{SP}$ values are expected to be very fast. To gain a clearer understanding of the giant PL intensity enhancement and the slower PL decay process in Pt metal capped ZnO, we propose a possible mechanism. Usually, electron-hole pairs generated in semiconductor materials decay through both radiative and nonradiative recombination processes. The PL decay time of bare ZnO (τ_{ZnO}) can be expressed as

$$\frac{1}{\tau_{ZnO}} = \frac{1}{\tau_{NR}} + \frac{1}{\tau_R}, \tag{1}$$

where τ_{NR} and τ_R represent the nonradiative and radiative decay time of bare ZnO, respectively. As is well known, there are many surface defect states in the bare ZnO (Ref. 14) and they often act as nonradiative recombination centers. As much of the laser absorption occurs at the surface (different from the case of excitation from the substrate), the PL decay of bare ZnO is dominated by nonradiative recombination and the decay time τ_{NR} is very short. After capped with Pt metal, the surface states were remarkably reduced by

SM,[15] in turn the nonradiative recombination rate decreases and radiative recombination increases. Therefore, the internal quantum efficiency and the band edge emission of ZnO can be enhanced by SM with Pt capping.[10,15] However, the different enhancement ratio between Pt NP/ZnO and Pt film/ZnO indicated that there exists a electron-hole-SP coupling in addition to SM. After Pt coatings, the PL decay time ($\tau_{\text{Pt-ZnO}}$) can be expressed as

$$\frac{1}{\tau_{\text{Pt-ZnO}}} = \frac{1}{\tau_{\text{NR}}^*} + \frac{1}{\tau_R^*} + \frac{1}{\tau_{\text{SP}}}, \quad (2)$$

where τ_{NR}^* and τ_R^* are the nonradiative and radiative decay times of ZnO capped with Pt metal, respectively. $1/\tau_{\text{SP}}$ is the electron-hole-SP coupling rate. Comparing Eq. (1) with Eq. (2), it can be observed that electron-hole-SP coupling will definitely increase the PL decay rate due to Pt coatings. Meanwhile, most radiative recombination occurred at the interior of the ZnO film, so the radiative recombination rate should be similar before and after Pt coatings ($\tau_R \approx \tau_R^*$). Notably, SM can remarkably decrease the nonradiative recombination rate ($1/\tau_{\text{NR}} \ll 1/\tau_{\text{NR}}^*$). So the PL decay rates of ZnO capped with Pt metal are even smaller than that of bare ZnO although there is an additional decay channel. As the thickness of Pt film has the same value with the maximum height of Pt NP (see Fig. 1), the average thickness of Pt film is a little larger than that of Pt NP. According to previous reports, the thicker metal coating can adjust the SP energy closer to that of the ZnO emission and hence increased the Purcell enhancement ratio.[6,8] Therefore, it can be concluded that Pt film/ZnO can realize larger Purcell factor and make the SP energy closer to the ZnO bandgap energy compared with that of Pt NP/ZnO. The Purcell enhancement factor (F_p) (Ref. 16) in this work can be expressed as[10]

$$F_p = \frac{\frac{1}{\tau_{\text{Pt-ZnO}}}}{\frac{1}{\tau_{\text{ZnO}}}} = \frac{\frac{1}{\tau_{\text{NR}}^*} + \frac{1}{\tau_R^*} + \frac{1}{\tau_{\text{SP}}}}{\frac{1}{\tau_{\text{NR}}} + \frac{1}{\tau_R}}. \quad (3)$$

As $F_{p(\text{Pt film/ZnO})}$ is larger than $F_{p(\text{Pt NP/ZnO})}$, and $1/\tau_{\text{Pt-ZnO}}$ of Pt film/ZnO is larger than that of Pt NP/ZnO, this implies that the decay rate of Pt NP/ZnO is slower than that of Pt film/ZnO. Meanwhile, $1/\tau_R^* + 1/\tau_{\text{NR}}^*$ has the similar value for both Pt NP/ZnO and Pt film/ZnO as mentioned above, so $1/\tau_{\text{SP}}$ of Pt film/ZnO should be larger than that of Pt NP/ZnO.

As for the stronger PL intensity of Pt NP/ZnO compared with that of Pt film/ZnO, we have given an interpretation in Fig. 4. There are three processes in the SP-mediated emission from the metal side:[4] (1) excitons or electron-hole pairs are generated in ZnO by He–Cd laser and the emission energy can transfer to the SP when the bandgap energy of ZnO is comparable to the electron vibration energy of SP at the metal/semiconductor interface, (2) energy from metal/semiconductor SP should be effectively transferred to the opposite air/metal surface SP, and (3) the energy can be extracted as light by scattering of SP at air/metal surface due to the surface roughness. However, if the metal surface is perfectly flat, the SP energy will be thermally dissipated. Because process (2) is only associated with the dielectric constant of air and ZnO,[4] this energy transfer between
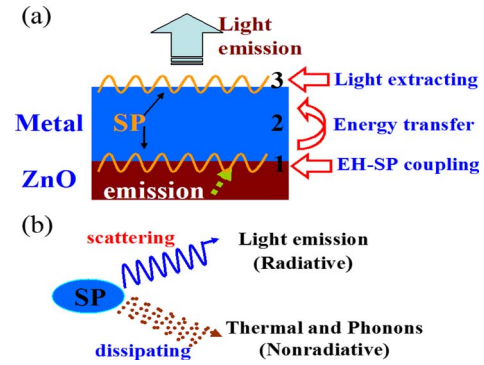

FIG. 4. (Color online) The schematic diagram for (a) enhancing the emission from the metal side via SP cross-coupling and (b) the radiative and nonradiative processes of SP by scattering and dissipating, respectively.

two surfaces should be the same for Pt NP/ZnO and Pt film/ZnO. For process (1), the emission energy for both Pt film/ZnO can have a little more efficient coupling with SP than that of Pt NP/ZnO due to $1/\tau_{\text{SP}}(\text{Pt film/ZnO}) > 1/\tau_{\text{SP}}(\text{Pt NP/ZnO})$, but this difference should not be obvious. For process (3), inherent Pt surface roughness of Pt film/ZnO can realize enhancement of bandgap emission from ZnO, but most of the SP energy have been thermally dissipated. As for the Pt NP capping, the demonstrated 12-fold enhancement of bandgap emission is attributed to fact that the periodic Pt NP can offer a large amount of scattering mediums, which enormously increase the light extraction efficiency.

In summary, we were able to enhance the bandgap emission of ZnO by incorporating Pt NP (12 folds) and Pt film (twofolds). These enhancements are mainly caused by the cross-coupling between spontaneous recombination in ZnO and SPs arising from Pt interfaces. TRPL results indicated that SM by Pt can largely reduce the nonradiative recombination rate, which, together with the efficient light extraction by Pt NP, accounts for additional mechanisms for the PL enhancement.

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