APPLIED PHYSICS LETTERS **96**, 071107 (2010)

Surface plasmon enhanced band edge luminescence of ZnO nanorods by capping Au nanoparticles

C. W. Cheng, E. J. Sie, B. Liu, C. H. A. Huan, T. C. Sum, H. D. Sun,[a] and H. J. Fan[a]
Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, 637371 Singapore, Singapore

(Received 16 December 2009; accepted 19 January 2010; published online 17 February 2010)

The author observe sixfold enhancement in the near band gap emission of ZnO nanorods by employing surface plasmon of Au nanoparticles, while the defect-related emission is completely suppressed. Time-resolved photoluminescence indicates that the decay process becomes much faster by Au capping. The remarkable enhancement of the ultraviolet emission intensities and transition rates is ascribed to the charge transfer and efficient coupling between ZnO nanorods and Au surface plasmons. The suppression of the green emission might be due to a combined effect of Au surface plasmon and passivation of the ZnO nanorod surface traps. © *2010 American Institute of Physics*. [doi:10.1063/1.3323091]

Surface plasmons (SPs), excited by the interaction between light and electron plasma waves at the metal surface,[1] has attracted intense scientific interest due to its applications in enhancement of the weak physical process, such as the absorption of light in molecules[2,3] and Raman scattering intensities.[4,5] Recently, SPs mediated emission has also been proven as an effective way to improve the quantum efficiency of light emitting materials and light emission diodes (LEDs).[6,7] Among direct band gap crystals, ZnO has a wide band gap of ~3.37 eV and large exciton binding energy of 60 meV at room temperature. Proof-of-concept demonstrations of photonic applications of ZnO nanorods are available such as ultraviolet lasers[8] and LEDs.[9] However, in most cases, a large number of carriers are trapped by defects or impurities inside luminescence centers, resulting in a low efficiency of the light emission. Hence, to obtain highly efficient ultraviolet emission from the near band edge is one of most important issues for photonic applications of ZnO. In the past few years, a number of studies have been conducted to improve the band edge emission from ZnO films and nanostructures by metal capping, and different metals (e.g., Ag, Au, Al, and Pt) have been used as capping layers.[10–18] However, there are relatively few publications that address the luminescence dynamics of ZnO/metal structures, and the correlation between SPs and the photoluminescence (PL) enhancement is in general not well documented.

In this letter, we have studied the PL properties of the bare and gold-capped ZnO nanorods. It is found that the band edge emission can be dramatically enhanced, while the defect-related emission is suppressed to the noise level. The intensity ratio of the band gap emission to the defect-related emission can be improved by up to 10^3 times. In addition, the band edge PL decay also becomes faster after the Au capping. A possible excitons coupling mechanism with the metal SPs will be discussed.

Vertical aligned ZnO nanorods were grown on GaN/sapphire substrates through a standard vapor-transport and deposition method as reported elsewhere.[19] The capping Au nanoparticles were deposited on ZnO nanorods using a dc sputtering system (JFC-1600, JEOL). The coverage of Au particles was controlled by using different sputtering time at a fixed current of 10 mA. PL measurements were performed by excitation from a 325 nm line of a continuous-wave He–Cd laser. For time-resolved PL (TR-PL) measurements, the sample was excited by 310 nm laser pulses generated from an optical parametric amplifier (Coherent TOPAZ™) that was pumped using a 100 fs, 1 kHz regenerative amplifier (Coherent Legend™). The TR-PL data were collected by an Optronis™ Optoscope streak camera combined with a high resolution charge-coupled device camera. All the data were obtained from the same ZnO sample, which was cut into four pieces for PL measurement before Au sputtering. We found that there was nearly no difference in the PL intensity for all four samples before the Au sputtering. Also the PL spectra were recorded at different positions on each sample in order to assure the change in PL intensity is not due to sample nonhomogeneity; we herein present the representative spectra. Moreover, all the PL data were collected under the same conditions (light path, excitation power, and acquisition time) to exclude any other effect on the PL intensity.

Figures 1(a) and 1(b) show the 20° tilted view SEM images of the bare ZnO nanorods and Au/ZnO nanorods with 50 s Au sputtering. The ZnO nanorods have a diameter of 60–70 nm and length of ~1 μm. Clearly, the bare ZnO nanorod has a smooth surface [Fig. 1(c)], while for the Au/ZnO after 50 s sputtering, Au nanoparticles with diameters of about 5 nm are uniformly distributed on the surface of the ZnO nanorod. Reasonably, the sizes of the Au particles for Au/ZnO with 20 and 100 s sputtering time are respectively smaller and larger than 5 nm.

Figure 2 shows the room temperature PL spectra of ZnO nanorods before and after Au sputtering. For the bare ZnO nanorods, a weak near band gap emission at around 378 nm and a broad and intense defect-related emission band centered at ~520 nm are observed, which are relatively common features for ZnO nanostructures. After the Au sputtering, it is found that the defect emission disappears for all the samples. Moreover, the band edge emission intensity is variably enhanced with Au sputtering, namely, the Au nanoparticle size. As shown, the enhancement factor reaches a maximum value for the sputter time of 50 s and then decreases.

---

[a] Electronic addresses: hdsun@ntu.edu.sg and fanhj@ntu.edu.sg.

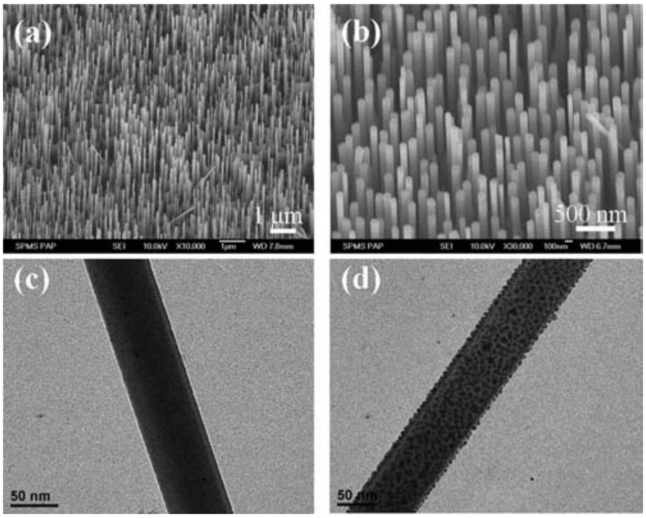

FIG. 1. 20° tilted view SEM image of (a) bare ZnO nanorods and (b) ZnO with Au capping by 50 s sputtering. (c) and (d) are TEM images of typical individual ZnO nanorod and Au/ZnO nanorod, respectively.

The band edge emission intensity of Au/ZnO with 50 s Au sputtering is nearly sixfold higher than that of bare ZnO nanorods, and the intensity ratio between the band edge and defect emission can be enhanced by up to 10^3 times. A small energy shift is also observed for the Au/ZnO with 20 s sputtering (curve 2 in Fig. 2).

To confirm the origin of the near band edge peaks, low temperature (10 K) PL measurement was conducted for both the bare ZnO nanorods and Au/ZnO samples (see Fig. 3). The most intense PL emission line at 3.358 eV is attributed to the excitons bound to neutral donors (denoted by D^0X). On the higher energy side of the D^0X line, the free exciton emission is observed at 3.376 eV. On the lower energy side, the peaks can be resolved by two electron satellite transitions[20] and up to four orders longitudinal optical (LO) phonon replicas of D^0X with an energy separation of ~72 meV. For the Au/ZnO nanorods [Figs. 3(b) and 3(c)], the spectra are similar to that of bare ZnO nanorods, except for the absence of the higher orders LO phonon replicas. It is expected that the surface modification by Au nanoparticles reduces the exciton-LO phonon interaction according to the Franck–Condon model.[21]

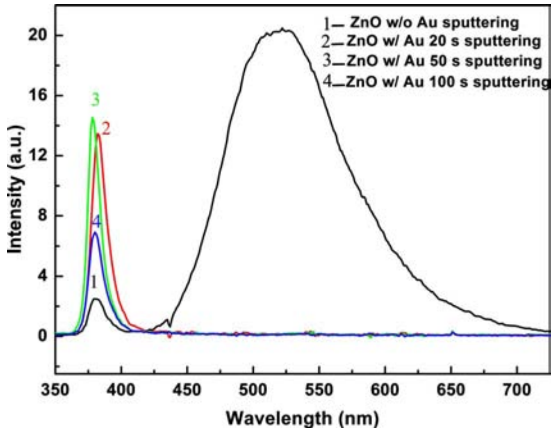

FIG. 2. (Color online) Room temperature PL spectra of ZnO without and with Au after different sputtering time.

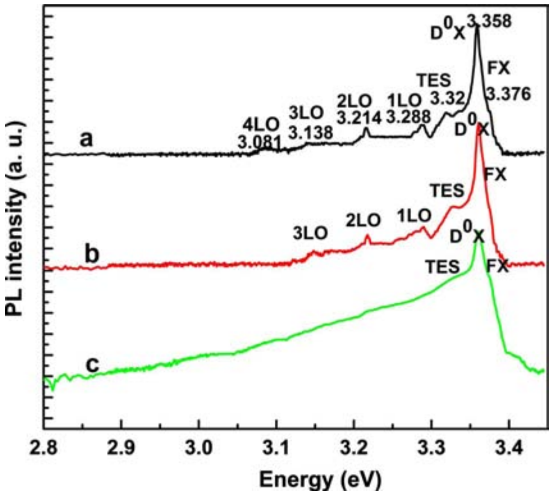

FIG. 3. (Color online) 10 K PL spectra of (a) bare ZnO, (b) Au/ZnO with 50 s sputtering, and (c) 100 s sputtering.

The increased band edge emission and complete suppression of defect emission are obviously related to the Au nanoparticles. In the ZnO community, the broad green emission is generally regarded to be related to surface defects such as oxygen vacancy (V_O) and/or Zn vacancy (V_{Zn}).[22] It has been reported that coating the ZnO surface with a layer of dielectric material such as Al_2O_3 (Ref. 23) or polymer[24] can lead to a reduction of the surface traps due to surface passivation effects. Accordingly, the separation of electrons and holes within the surface depletion region is reduced, which means that more electron-hole pairs are generated. As a result, the band edge emission can be enhanced while the green emission is suppressed. We have seen similar results but will not repeat the data here. In the present experiment, after the deposition of Au nanoparticles, there might also be such surface passivation effect. However, the surface passivation effect is expected to be small and it alone cannot explain our observations. In our experiment, the green emission disappears for all the samples whereas the reduction in defect emission intensity by surface passivation is generally small. As a matter of fact, a metal layer coating is far more complicated than a simple dielectric or polymer coating;[23,24] in the former cases, there exists surface plasmon polaritons caused by a direct exciton-plasmon coupling between excitons of the ZnO nanorods and SPs of Au nanoparticles. We will discuss in the following that the enhancement of band edge emission mainly arises from the SPs coupling.

TR-PL measurements were performed to gain more insights of the coupling mechanism. Figure 4 shows the room temperature TR-PL of bare and two types of Au-capped ZnO nanorods (50 and 100 s Au sputtering). The fitting of these TR-PL decay curves involves a deconvolution between the instrument response function (<20 ps) and a monoexponential radiative decay. The decay lifetime τ, is defined such that the ideal radiative decay curve goes as:$I_{(t)}=Ae^{-t/\tau}$, where A is the normalization constant. It can be seen that the Au/ZnO samples have faster decay processes than the bare ZnO. The fitted decay times are ~35 ps for 50 s-sputtered and ~30 ps for 100 s-sputtered sample, respectively, whereas ~230 ps for the bare ZnO nanorods. These observations are in agreement with previous reports on SPs coupling with InGaN quantum wells.[6,7] The PL decay time of bare ZnO (τ_{ZnO}) can

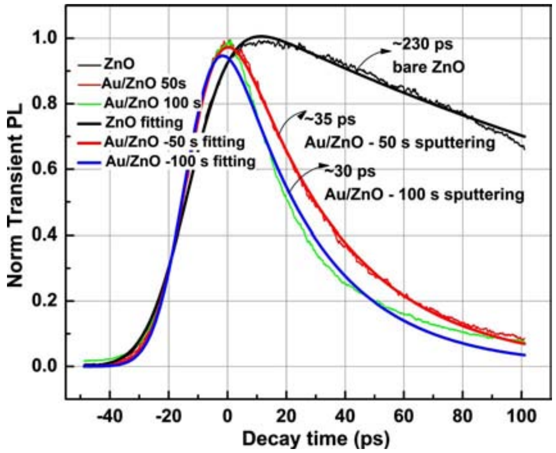

FIG. 4. (Color online) Representative room temperature TR-PL decays of bare ZnO, Au/ZnO with 50 s sputtering, and Au/ZnO with 100 s sputtering.

be expressed as $(1/\tau_{\mathrm{ZnO}})=(1/\tau_{\mathrm{NR}})+(1/\tau_{\mathrm{R}})$, where τ_{NR} and τ_{R} represent the nonradiative and radiative decay time of bare ZnO. After being capped with Au metal, due to the SPs coupling, a new recombination path is created. The decay time $(\tau_{\mathrm{ZnO-Au}})$ is then modified to be $(1/\tau_{\mathrm{ZnO-Au}})=(1/\tau^{*}_{\mathrm{NR}})+(1/\tau^{*}_{\mathrm{R}})+(1/\tau_{\mathrm{SP}})$ where τ^{*}_{NR} and τ^{*}_{R} are nonradiative and radiative decay times of Au-capped ZnO, respectively, and $1/\tau_{\mathrm{SP}}$ is the exciton-SP coupling rate. As τ_{SP} is expected to be very small, the spontaneous emission rate of Au/ZnO is much faster than that of bare ZnO nanorods. The Purcell enhancement factor F_{P} quantifies the increase in spontaneous emission rate into a mode of interest, and can be derived from the measured TR-PL decay time as follows: $F_{\mathrm{P}(\varpi)}=\tau_{\mathrm{PL}(\varpi)}/\tau^{*}_{\mathrm{PL}(\varpi)}=K^{*}_{\mathrm{PL}(\varpi)}/K_{\mathrm{PL}(\varpi)}$, where $K_{\mathrm{PL}(\varpi)}$ and $K^{*}_{\mathrm{PL}(\varpi)}$ are the original and enhanced PL decay rate, respectively. Using $\tau_{\mathrm{PL}(\varpi)}=230$ ps and $\tau^{*}_{\mathrm{PL}(\varpi)}=35$ ps, an approximate 6.6 time enhancement of the spontaneous emission rate is calculated for the 50 s sputtered sample. Based on the above results, we expect that an efficient energy transfer occurring between the Au nanoparticles and ZnO nanorods is due to exciton-SPs coupling.

We propose there are two distinct physical processes that account for the band edge emission enhancement. First, it is due to charge transfer, as proposed in earlier reports.[12,14,16] The energy level of defect states with respect to the vacuum level in ZnO (−4.99 eV) is close to the Au Fermi level (−5.3 eV).[25] This means flow of electrons from the ZnO defect level into the Au Fermi level is allowed, which increases the electron density within the Au.[14] Consequently, hot electrons are created in high energy states which can transfer back to the conduction band of ZnO nanorods. In other words, electrons in the defect states are pumped via Au to the conduction band of ZnO. Hence, PL intensity of the band gap emission is enhanced and in parallel the defect emission is suppressed. Second, the TR-PL results indicate the Purcell enhancement of the ZnO band edge emission by Au SPs. In addition, we found that the band edge emission is also drastically enhanced by introduction of a 5 nm Al_2O_3 layer between the ZnO nanorod and Au (in this case, a charge transfer is not allowed. Data are not shown here). Thus, we argue that a coupling between ZnO excitons and Au SPs exists and has led to the UV emission enhancement. With the sputter time increasing from 50 to 100 s, the Au particles grew larger and formed a continuous film. In this case, the adsorption process will dominate over the scattering so that radiation as photons into free space will be suppressed due to nonradiative dissipation of the surface plasmon. This explains the attenuation of light emission for the ZnO/Au after 100 s sputtering in Fig. 2.

Regarding the complete suppression of visible emission, in addition to the aforementioned transfer of electrons in the ZnO defect levels to Au, the other process, as proposed earlier,[14] is also possible: the visible emission of ZnO may be resonantly absorbed by Au since the emission energy (∼500 nm) closely match the absorption peak of 5 nm Au nanoparticles.

In summary, we have shown great enhancement of band edge emission of ZnO nanorods by incorporating Au nanoparticles, while the defect emission of the nanorods are completely suppressed. It is believed that these changes are mainly caused by the coupling between spontaneous emission in ZnO and SPs from the Au, although a small contribution due to surface passivation effect cannot be ruled out. TR-PL results indicate that the Au nanoparticles can greatly increase the spontaneous emission rate due to the formation of surface plasmon polaritons.

[1] T. W. Ebbesen, H. J. Ghasemi, H. F. Thio, and P. A. Wolff, Nature (London) **391**, 667 (1998).
[2] J. Dintinger, S. Klein, and T. W. Ebbesen, Adv. Mater. (Weinheim, Ger.) **18**, 1267 (2006).
[3] D. M. Schaadt, B. Feng, and E. T. Yu, Appl. Phys. Lett. **86**, 063106 (2005).
[4] S. M. Nie and S. R. Emery, Science **275**, 1102 (1997).
[5] X. H. Huang, I. H. El-Sayed, W. Qian, and M. A. El-Sayed, Nano Lett. **7**, 1591 (2007).
[6] K. Okamoto, I. Niki, A. Shvartser, Y. Narukawa, T. Mukai, and A. Scherer, Nature Mater. **3**, 601 (2004).
[7] K. Okamoto, I. Niki, A. Scherer, Y. Narukawa, T. Mukai, and Y. Kawakami, Appl. Phys. Lett. **87**, 071102 (2005).
[8] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, Science **292**, 1897 (2001).
[9] J. H. Lim, C. K. Kang, K. K. Kim, I. K. Park, D. K. Hwang, and S. J. Park, Adv. Mater. (Weinheim, Ger.) **18**, 2720 (2006).
[10] P. Cheng, D. Li, Z. Yuan, P. Chen, and D. R. Yang, Appl. Phys. Lett. **92**, 041119 (2008).
[11] D. Y. Lei and H. C. Ong, Appl. Phys. Lett. **91**, 211107 (2007).
[12] M. K. Lee, T. G. Kim, W. Kim, and Y. M. Sung, J. Phys. Chem. C **112**, 10079 (2008).
[13] J. B. You, X. W. Zhang, Y. M. Fan, Z. G. Yin, P. F. Cai, and N. F. Chen, J. Phys. D **41**, 205101 (2008).
[14] H. Y. Lin, C. L. Cheng, Y. Y. Chou, L. L. Huang, Y. F. Chen, and K. T. Tsen, Opt. Express **14**, 2372 (2006).
[15] J. Li and H. C. Ong, Appl. Phys. Lett. **92**, 121107 (2008).
[16] Y. Zhang, X. H. Li, and X. J. Ren, Opt. Express **17**, 8735 (2009).
[17] K. W. Liu, Y. D. Tang, C. X. Cong, T. C. Sum, A. C. H. Huan, Z. X. Shen, L. Wang, F. Y. Jiang, X. W. Sun, and H. D. Sun, Appl. Phys. Lett. **94**, 151102 (2009).
[18] J. M. Lin, H. Y. Lin, C. L. Cheng, and Y. F. Chen, Nanotechnology **17**, 4391 (2006).
[19] H. J. Fan, A. Barnard, and M. Zacharias, Appl. Phys. Lett. **90**, 143116 (2007).
[20] A. Teke, Ü. Özgür, S. Dogan, X. Gu, H. Morkoç, B. Nemeth, J. Nause, and H. O. Everitt, Phys. Rev. B **70**, 195207 (2004).
[21] B. D. Bartolo and R. Powell, *Phonon and Resonance in Solids* (Wiley, New York, 1990).
[22] B. Q. Cao, W. P. Cai, and H. B. Zeng, Appl. Phys. Lett. **88**, 161101 (2006).
[23] J. P. Richters, T. Voss, D. S. Kim, R. Scholz, and M. Zacharias, Nanotechnology **19**, 305202 (2008).
[24] J. P. Richters, T. Voss, L. Wischmeier, I. Rückmann, and J. Gutowski, Appl. Phys. Lett. **92**, 011103 (2008).
[25] X. Yong and A. A. S. Martin, Am. Mineral. **85**, 543 (2000).