Enhancement of band gap emission stimulated by defect loss

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Abstract: Defect radiation has been always considered as the most important loss for an emitter based on band gap emission. Here, we propose a novel approach which goes against this conventional wisdom. Based on the resonance effect between the surface plasmon of metal nanoparticles and defect emission, it is possible to convert the useless defect radiation to the useful excitonic emission with a giant enhancement factor. Through the transfer of the energetic electrons excited by surface plasmon from metal nanoparticles to the conduction band of the emitter, the band gap emission can be greatly enhanced, while the defect emission can be suppressed to noise level.

OCIS codes: (240.6490) Spectroscopy, surface; (240.6680) Surface plasmons; (260.2501) Fluorescence.

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1. Introduction

The influence of solid state emitters on the daily life of human beings has been no less than spectacular. The needs for efficient lighting range from display, traffic signs, telecommunications, and aerospace to consumer products. Currently, worldwide resources have been devoted to searching for next generation lighting [1]. In applications for a solid state emitter, it is quite important to have high quantum efficiency without energy loss to the defects which inevitably present in solid state materials. However, for most materials used, in addition to band gap emission, an intense and broad defect radiation is generally found [2-5]. The control of defects is therefore the most important issue for the improvement of emission efficiency. Here, we present a novel approach in which a giant enhancement of band gap emission has been demonstrated at the expense of defect radiation. In our designed materials the defect transition is utilized to induce surface plasmon resonance due to the energy match between the defect emission and the surface plasmon of metal nanoparticles. The energetic electrons caused by the excitation of the surface plasmon can transfer from metal nanoparticles to the conduction band of semiconductor nanocrystals and recombine with holes in the valence band, as a result the excitonic emission is greatly enhanced.

Quite interestingly, by implementing our approach to the composite of ZnO nanorods and Au nanoparticles, the excitionic emission can be enhanced by as large as about twenty times, while the defect emission is suppressed to the level of our detection limit. The integrated intensity ratio between the excitonic emission and the defect emission can be improved from 0.016 to about 430, which is more than a factor of 10^4 enhancements. Furthermore, the composite of GaN nanowires and metal nanoparticles has also been tested, and the results have been found to be consistent with the prediction based on the underlying physics as we proposed.

2. Experiment

ZnO nanorods were grown by a solid-liquid-vapor process [6]. A mixture of high purity ZnO and carbon powders (the molar ratio is 1:1) was used for the growth. The powders were placed in an alumina boat, and loaded to the center of a tube furnace. The gold-coated sapphire substrate was placed in the same boat with the mixed powders. The distance between the mixed powders and the substrate was about 3 cm. Argon was then introduced into the system with a flow rate of 200 sccm as the carrier gas. Afterwards, the tube was heated to 980 °C at a rate of 40 min^{-1}. The reaction lasted about 60 min. After the furnace cooled down, white and grayish-white color products formed on the surface of the sapphire substrate. A sputtering system was used to deposit Au particles on ZnO nanorods. The coverage of Au particles was controlled by a current of 20 mA for different deposition time with 10 s, 20 s, 35 s, 50 s, 60 s, and 75 s. Under our deposition condition, the deposition rate of the Au film is about 0.29 nm/sec.

The morphology and component of ZnO nanorods were characterized by scanning electron microscopy (SEM) (JSM 6500, JEOL) and electron energy dispersion X-ray (EDX) (Oxford). Photoluminescence (PL) spectra of ZnO nanorods were performed by the excitation from a 325 nm He-Cd laser at room temperature. Cathodoluminescence (CL) spectra were performed by Gatan MonoCL3 with electron acceleration voltages from 5 keV to 20 keV.

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3. Results and discussions

Figure 1(a) shows the top view SEM image of ZnO nanorods, and Figure 1(b) is the SEM image at a tilt angle of 20°. The ZnO nanorods form a well organized hexagonal shape grown on sapphire (α-plane) with diameter of 90 to 160 nm, and a length of about 2 μm. EDX analysis reveals the molecular ratio of the ZnO nanorods to be: 60.29 % Zn and 39.71 % O. Figures 1(c) and 1(d) show SEM images of ZnO nanorods with and without the coverage of Au particles deposited by a current of 20 mA for 35 s.

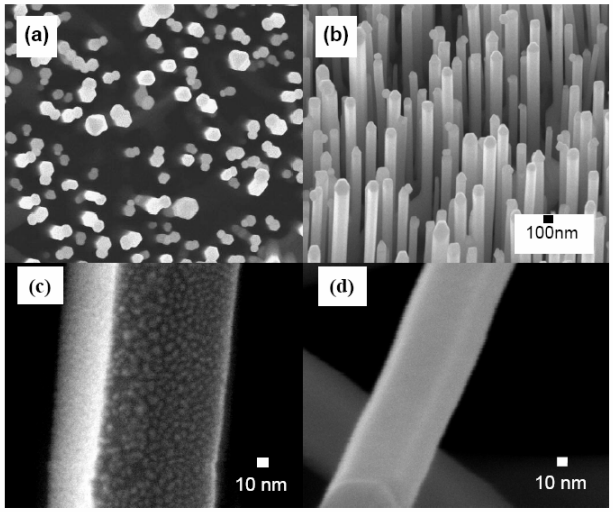

Fig. 1. Scanning electron microscopy images of (a) top-viewed, (b) tilt angle of 20° ZnO nanorods grown on sapphire, (c) ZnO nanorods with the coverage of gold nanoparticles deposited by a current of 20 mA for 35 s, and (d) ZnO nanorods.

Figure 2 shows the PL spectrum of ZnO nanorods excited by a CW He-Cd laser. It consists of a weak, excitonic ultraviolet (UV) emission at 384 nm and a relatively strong defect emission at 500 nm due to oxygen vacancy and zinc interstitials [6-8]. It is well known that the control of defect states is the most important issue for the enhancement of emission efficiency. There were several attempts to suppress the defect loss and enhance the excitonic emission, but only with limited successes [9,10]. Here, we provide a simple approach to overcome this difficulty by coating gold nanoparticles on the surface of nanostructures. As the gold nanoparticles were coated with 20 mA for 20 s on the ZnO nanorods, the PL result displays a very strong enhancement of excitonic emission and the defect emission is reduced to our detection limits as shown in Fig. 2. Similar to the effect of hydrogen doping method [10], a simple mechanism to interpret out result is that the deposited gold atoms can passivate the defect states, thereby enhance the band gap emission. However, this straight forward explanation fails to account for the result shown below, in which the enhancement factor of excitonic emission reveals a wide variation with the increasing coating time.

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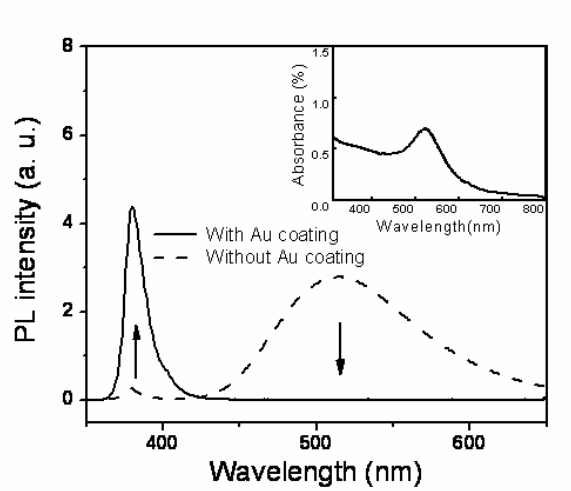

Fig. 2. Photoluminescence spectra of ZnO nanorods with and without Au coating. The coverage of Au particles was deposited by a current of 20 mA for 20 s. The inset shows the absorption spectrum of a typical surface plasmon extinction spectrum of Au nanoparticles.

In order to search for the optimum condition of the enhancement of the band gap emission, we have deposited Au particles for different coating time. The tendency of the enhancement factor of the excitonic emission reveals a much more complicated picture than that of the suppression factor of the defect emission as shown in Figs. 3(a) and 3(b). For all the Au particles coated with different deposition time, the defect emission is almost undetectable. When the coating time increases from 10 s to 35 s, the enhancement factor of the band gap emission increases. At the coating time of 50 s, the enhancement factor drops, and there exists a maximum enhancement as the coating time increases to 60 s. Finally, as the coating time reaches 75 s, the enhancement factor drops again. Similar tendency has also been obtained from CL measurement with different electron acceleration voltage as shown in Fig. 3(c).

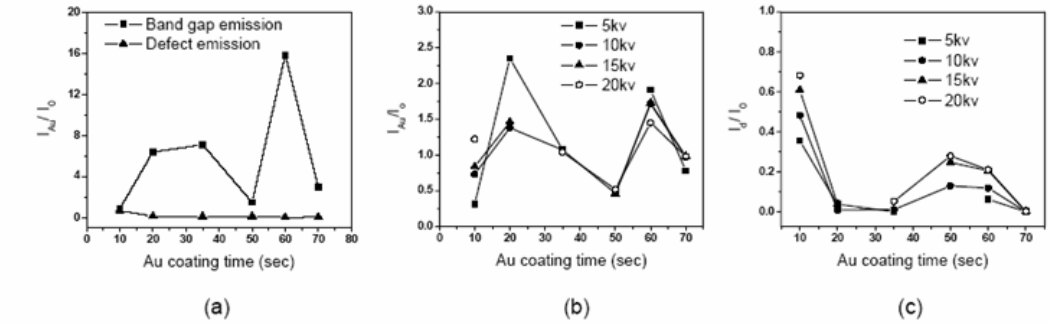

Fig. 3. (a) Coating time dependence of relative intensity ratio of excitonic and defect emission. The square (■) denotes the ratio of integrated intensity of excitonic emission of ZnO nanorods with gold coating (I_{Au}) to that of non-coated sample (I_0). The triangle (▲) denotes the intensity ratio of defect emission with Au coating to that of non-coating defect emission. (b) Coating time dependence of relative integrated intensity ratio of (a) (I_{Au}/I_o): excitonic emission, (c) (I_d/I_0): defect emission of ZnO nanorods with four different electron acceleration voltages.

To resolve the involved mechanism, the optical properties of gold nanoparticles have been performed. A strong absorption around 520 nm due to surface plasmon resonance is

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observed as shown in the inset of Fig. 2. Quiet interestingly, the photon energy of the defect emission is very close to that of the surface plasmon resonance of Au nanoparticles. This coincidence motivates us to propose the underlying mechanism responsible for the giant enhancement of the band gap emission as follows. Au particle is an excellent absorber for the defect emission due to surface plasmon resonance, which leads to the suppression of the defect emission. After the resonant excitation, particle plasmons can undergo a nonradiative decay via excitation of electron-hole pairs, and create energetic electrons in higher energy states [11]. The energetic electrons in Au nanoparticles are able to transfer from Au particle to the conduction band of ZnO nanorods. The electrons then relax extremely fast with subpicosecond time scales [12] and rapidly recombine with holes in the valence band with a time constant of about 10 ns [13]. Therefore, it is possible to greatly enhance the band gap emission through the effect of surface plasmon resonance stimulated by the defect transition. Here, it is worth noting that the existence of energetic electrons in metal particles is a result of the interaction between surface plasmon and electron [14]. Even if the plasmon represents the collective motion and its energy is distributed amongst the Fermi gas, it is quite possible to have a single electron excitation through nonradiative decay of the plasmon [15].

To illustrate and obtain a clearer picture for the enhancement of the excitonic emission, the underlying mechanism is plotted in Fig. 4. In drawing the band alignment, we have used the data, in which the conduction band of ZnO is located at -0.8 V vs normal hydrogen electrode (NHE), and the Fermi level of gold is at 0.75 V vs NHE [16,17]. We can clearly see that the defect emission from ZnO nanorods can be used to excite the surface plasmon of Au particles. After the occurrence of surface plasmon resonance, the excited electrons in Au particles stay in higher energy states, and they are able to transfer to the conduction band of ZnO nanorods. Additional radiative band gap transitions can be obtained, when the excited electrons recombine with holes in the valence band. Therefore, the defect emission is effectively suppressed and the band gap emission is greatly enhanced.

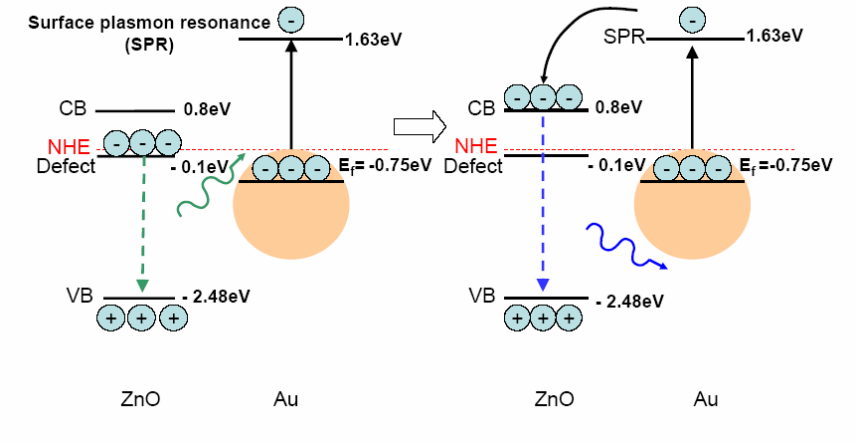

Fig. 4. Schematics of the effect of surface plasmon resonance on suppression and enhancement of defect and excitonic emissions, respectively.

According to our proposed mechanism, the complicate variation of the enhancement factors versus the coating time of Au is readily understood. In the beginning, the increase of the enhancement factor with the coating time is due to the increase of Au particle density. At the coating time of 50 s, the drop of the enhancement factor is because the emission is

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strongly scattered due to the high density of Au particles. This interpretation was supported by the fact that the enhancement factor of PL spectrum is much larger than that of the micro PL spectrum (which is not shown here) because the angle of the detected emission in micro PL measurement is much smaller than that of PL measurement. This result has been further confirmed by changing the detection angle in PL measurement. When the coating time is 60 s, the enhancement factor has the maximum value. It is attributed to the fact that the coverage under this condition, the density of the Au particles is optimized, which provides the most efficient way for the excited electrons transfer from Au surface to the conduction band of ZnO nanorods. Finally, as the Au film is too thick, the emissions from ZnO nanorods are densely shadowed by the Au film, and the emissions drop again. We thus can see that the optimum condition is a consequence of a combination of several factors.

In order to confirm that the observed enhancement of the excitonic emission is indeed at the expense of the defect radiation, another ZnO nanorod sample with negligible defect emission was used to examine the above scheme. After coating Au nanoparticles on the ZnO nanorods, the excitonic emission decreases as shown in Fig. 5. This behavior can be understood by the fact that without surface plasmon resonance induced by defect emission, the electrons in Au particles are not able to reach to higher energy states and they can not transfer from gold to the conduction band of ZnO nanorods. In this case, electron transfer from the conduction band of ZnO nanorods to Au nanoparticles dominates the process, and hence the band gap emission is reduced, which has been observed in several previous reports [18].

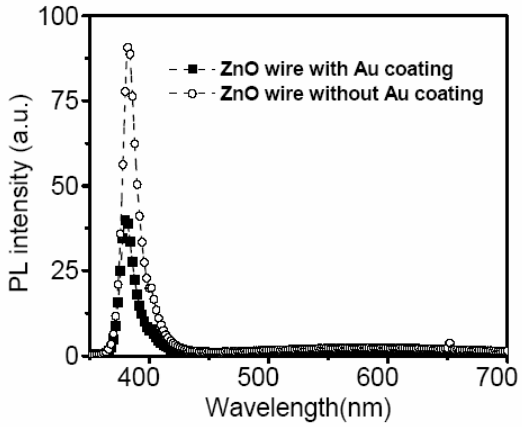

Fig. 5. Photoluminescence spectra of ZnO nanorods with Au coating (20 mA, 60 s) and without Au coating.

To further test our proposed mechanism, we have performed similar experiments on GaN nanowires. The results are shown in Fig. 6(a). Unlike the results of ZnO nanorods, both of the defect and band gap emission are suppressed under all different Au coverage. According to the above mechanism, this result can be understood by the fact that the energy of the defect emission (625 nm = 1.98 eV) is well below the surface plasmon energy (520 nm = 2.38 eV) of Au particles. It can not be used to efficiently excite surface plasmon, and hence there is no additional contribution to the band gap emission. Instead, the transfer of the photoexcited electrons from GaN nanowires to the Fermi-level of Au particles becomes dominant. Thus, both of the defect and band gap emission are quenched. However, with the spray of gold nano-ellipsoids solution into GaN nanowires, the band gap emission can be

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enhanced by several times, while the defect emission was normalized to that of the as-grown sample (as shown in Fig. 6(b)). It is well known that the surface plasmon of a metallic ellipsoid contains two eigenmodes, and their frequencies can be manipulated by the aspect ratio of the ellipsoid. It is our intention to choose the gold ellipsoid with surface plasmon that can absorb the photons emitted from the defect states of GaN nanowires as shown in the inset of Fig. 6(b). This result demonstrates that our proposed principle does work well for the case of GaN nanowires as well. Our experimental results therefore demonstrate that through the intrusion of Au nanoparticles, it is possible to obtain a large enhancement of band gap emission at the expense of defect transition.

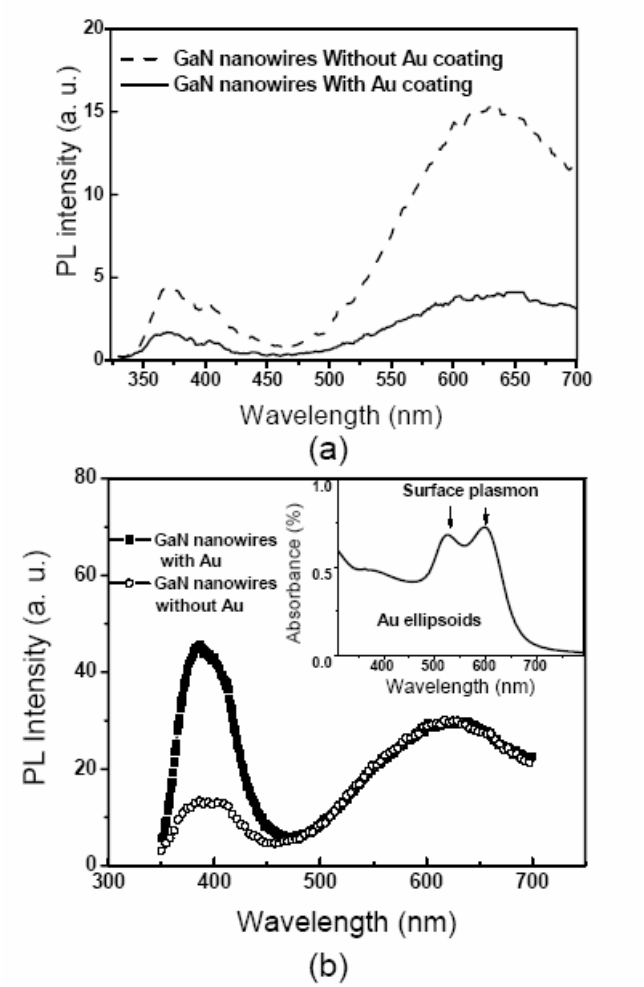

Fig. 6. (a) Photoluminescence spectra of GaN nanowires with Au coating (20 mA, 60 s) and without Au coating. The Au coating was performed by a current of 20 mA for 60 s, (b) Photoluminescence spectra of GaN nanowires with (the square ■) and without Au nano-ellipsoids (the circle ○). The spectra are normalized to their defect emission intensities. The inset is the absorbance spectrum of gold ellipsoid solution.

4. Conclusion

In summary, in addition to the surface modification, we have presented an effective approach

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for simultaneously suppressing defect emission and enhancing band gap emission by defect induced surface plasmon resonance. Quite remarkably, the integrated intensity ratio between excitonic and defect emission of ZnO nanorods can be enhanced by a factor as large as 10^4. One of the unique behaviors here is that energy associated with the defect transition can be effectively transferred to the useful band gap emission. The novel mechanism discovered here goes against the conventional wisdom that defect recombination is always considered as a major loss for band gap emission. Besides the examples shown here, the idea of this approach has a great impact on the optoelectronics. In that, it can be used as a general method for preparing high-efficiency optoelectronic devices, utilizing the following key concepts: (i) The resonant transition energy of metal nanoparticles coincides with the photon energy of defect emission. This condition is not difficult to fulfill for the case of surface plasmon resonance because plasmon energy can be tuned by the size and the shape of metal nanoparticles. (ii) The band alignment satisfies the condition that the energy offset between the conduction band edge of semiconductor nanocrystal and the Fermi energy of metal is less than surface plasmon energy. (iii) Metal coverage is chosen such that the enhancement factor is optimized.

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