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Giant enhancement of bandgap emission of ZnO nanorods by platinum nanoparticles

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Abstract

By the formation of ZnO and Pt nanocomposites, it is found that the bandgap emission can be greatly enhanced, while the defect emission is suppressed to the noise level. The photoluminescence intensity ratio between the bandgap and defect emission can be improved by up to 10^3 times. The underlying mechanism behind enhancement of the bandgap emission and quenching of the defect emission is a combination of the energy transfer between defects and surface plasmon resonance in Pt nanoparticles, as well as electron–hole pair generation and recombination in the ZnO nanorods. Our results will be very useful to manufacturers of highly efficient optoelectronic devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the need to save energy resources has become an important issue in modern times, how to make highly efficient lighting is more and more requisite nowadays. For materials used in solid state emitters, it is well known that a large number of carriers are usually trapped by defects inside a luminescent centre that results in a low efficiency of the emitted light [1]. Hence, how to control the influence of defect states is the most important issue for the improvement of emission efficiency. Numerous studies have been conducted to improve the bandgap emission in semiconductors [2–6]. However, the results were not very successful. Here, we present an alternative approach where the defect emission was suppressed almost completely and the bandgap emission was enhanced considerably.

Our approach is based on the quantum particle coupling in metal–semiconductor nanocomposites. In addition to surface modification, the underlying mechanism involves the resonant coupling between the bandgap emission of semiconductor nanostructures and the surface plasmon in metal nanoparticles. The electron–hole pairs generated within the semiconductor through the resonant coupling at the metal/semiconductor interface will provide a strongly enhanced radiative recombination due to the increase in

density of states and spontaneous emission rate. Besides, the electrons in the defect states can transfer to the Fermi level of metal nanoparticles, and the defect emission is therefore suppressed. Interestingly, by implementing our approach to the composite of ZnO nanorods and Pt nanoparticles, the bandgap emission can be greatly enhanced, while the defect emission is suppressed to the level of our detection limit. For instance, the intensity ratio between bandgap and defect emission can be enhanced by up to 10^3 times. Due to its wide bandgap of 3.37 eV and high excitonic binding energy of 60 meV that is much greater than the thermal energy of 25 meV at room temperature, ZnO has attracted considerable attention recently for the fabrication of short wavelength optoelectronic devices, such as light-emitting diodes (LEDs) and laser diodes [7, 8].

2. Experiment

ZnO nanorods were grown by a vapour–liquid–solid process [9]. 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 centre 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.

Figure 1. Scanning electron microscopy images of (a) top-viewed, (b) tilt angle of 20° ZnO nanorods, (c) ZnO nanorods with the coverage of platinum nanoparticles deposited by a current of 20 mA for 105 s, and (d) ZnO nanorods without platinum nanoparticles.

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 °C min⁻¹. The reaction lasted for about 60 min. After the furnace cooled down, white and greyish-white colour products formed on the surface of the sapphire substrate. A sputtering system (JFC-1600, JEOL) was used to deposit Pt nanoparticles on ZnO nanorods and quartz slides. The coverage of Pt nanoparticles was controlled by a current of 20 mA for different sputtering times. Under our sputtering condition, the deposition rate of the Pt film is about 0.15 nm s⁻¹. When the sputtering time is less than about 100 s, the deposited Pt film is discontinuous, consisting of many nanoclusters, which were referred to as Pt nanoparticles. The size of Pt nanoparticles can be controlled by the sputtering time. For instance, at a sputtering time of 60 s, the average particle size is about 4–5 nm, and 7–8 nm for a sputtering time of 105 s.

The morphology and composition of ZnO nanorods were characterized by scanning electron microscopy (SEM) (JSM 6500, JEOL) and energy dispersive x-ray spectrometer (EDX) (Oxford). Photoluminescence (PL) spectra of ZnO nanorods were performed by the excitation from a 325 nm He–Cd laser. The radiative emission was dispersed by a Spex 0.85 m double-grating monochromator and detected by a cooled photomultiplier tube (PMT). The absorption spectra of platinum nanoparticles were detected with a Jobin-Yvon H10 spectrophotometer with a resolution of 1 nm, and a 100 W Xe lamp was focused onto the sample with a condenser, where the illumination light is unpolarized to excite all plasmonic response directions simultaneously.

3. Results and discussion

Figure 1(a) is 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 (*a*-plane) with diameter of 90–160 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)

Figure 2. Photoluminescence spectra of ZnO nanorods with and without Pt nanoparticles. The coverage of Pt nanoparticles was sputtered by a current of 20 mA for 60 s. The result clearly shows that the photoluminescence intensity ratio between the bandgap and defect emission can be improved by up to 10³ times.

and (d) show the SEM images of ZnO nanorods with 105 s sputtered Pt nanoparticles and without Pt nanoparticles. With a careful inspection, we can surely see that there are Pt nanoparticles on the surface of ZnO nanorods.

Figure 2 shows the PL spectra of ZnO nanorods without and with Pt nanoparticles. Before sputtering Pt nanoparticles on ZnO nanorods, we can see a rather weak bandgap emission around 380 nm, and a strong broad band defect emission around 520 nm. It is known that the defect emission arises from oxygen vacancies localized at the ZnO surface [9–12]. Quite surprisingly, after sputtering Pt nanoparticles, a great enhancement of the bandgap emission is observed, while the defect emission disappears and is below the detection limit. The intensity ratio between the bandgap and defect emission can be enhanced by up to about 10³ times.

The increase in the bandgap emission can be attributed to surface modification by Pt nanoparticles sputtered on ZnO nanorods. As reported previously [9–12], oxygen vacancy localized at ZnO surface is responsible for the defect emission at 520 nm. After depositing Pt nanoparticles on the surface of ZnO rods, they can fill the oxygen vacancies, and the defect structure is changed. As a consequence, it is unable to trap electrons again, thus the defect emission is suppressed. Meanwhile, more energetic electrons in the conduction band recombine with the holes in the valence band, and the enhancement of the bandgap emission thus occurs. However, this simple explanation fails to interpret the result as shown in figure 3, in which the intensity of the defect emission remains almost the same after the sputtering of more Pt nanoparticles, while the bandgap emission is greatly enhanced. This shows that the enhanced bandgap emission does not solely arise from the suppression of the defect emission.

In order to resolve the above puzzle, we have performed the optical absorption spectra of Pt nanoparticles with different sputtering times as shown in figure 4. For all different sputtering times, a rather strong absorption band around the bandgap emission of ZnO nanorods at 380 nm has been found; it becomes more pronounced as the sputtering time is increased. According to the previous reports [13–17],

Figure 3. Photoluminescence spectra of ZnO nanorods before and after sputtering more Pt nanoparticles.

Figure 4. The absorption spectra of Pt nanoparticles with different sputtering times, of 15, 30, 45, 60, 75, 90 and 105 s.

the absorption band may be related to the surface plasmon resonance and interband transitions of Pt nanoparticles. These spectra provide an important clue for the understanding of the increased PL intensity as observed in figure 3. The mechanism involves the energy transfer between the metal nanoparticles

and semiconductor nanostructures [5, 18, 19]. The energy transfer can be greatly enhanced through the resonant coupling when the emitted photon energy of electron-hole (EH) pairs in the ZnO nanorods is equal to the energy of surface plasmon resonance (SPR) in Pt nanoparticles. With the strong coupling, surface plasmons can increase the density of states and the spontaneous emission rate in the ZnO nanorods [19], and lead to the enhancement of the radiative bandgap (BG) emission.

To illustrate the above-mentioned mechanism, a schematic diagram is plotted in figure 5. In drawing the band alignment, we have used the data, in which the conduction band of ZnO is located at -4.19 eV versus absolute vacuum scale (AVS), and the Fermi level of platinum is at -5.10 eV versus AVS [20, 21]. The suppression of defect emission can be explained in terms of the band alignment. It is known that the broad defect emission band arises from the defect level to the valence band [10, 11]. Since the defect level is very close to the Pt Fermi level, the electrons in the defect level can easily flow into the Pt Fermi level, as shown in figure 5. Therefore, with the strong resonant surface plasmon coupling, it will give rise to an enhanced interband transition where electrons from the conduction band combine radiatively with the holes in the valence band, resulting in an increased PL intensity of bandgap emission and a subsequent decrease of the defect emission.

To have a more complete understanding of the optical properties of Pt and ZnO nanocomposites, the dependence of the bandgap and the defect emission on Pt sputtering time are shown in figure 6. We can see that the longer the sputtering time, the greater the enhancement factor of the bandgap emission for the time interval $0 < t < 45$. It maximizes at about 45 s of the Pt sputtering time, and then starts to decline gradually with sputtering time. Conversely, the defect emission declines rapidly with sputtering time in the first 20 s, and then it decreases gradually with sputtering time. The decrease of the PL intensity of the bandgap emission at longer Pt sputtering time can be attributed to the shielding of the emitted light by the high density of Pt nanoparticles.

4. Conclusions

In summary, we were able to enhance the bandgap emission of ZnO nanorods by incorporating Pt nanoparticles,

Figure 5. The schematic diagram for the coupling between bandgap and surface plasmon resonance, and carriers transfer between the defect level and the Pt Fermi level. It results in enhanced bandgap emission and suppressed defect emission.

Figure 6. Sputtering time dependence of the bandgap and defect emission. The circle (○) denotes the intensity ratios of the bandgap emission (I_B) of ZnO nanorods with respect to that of the ZnO nanorods without Pt nanoparticles (I_{B0}). The triangle (△) denotes the intensity ratios of the defect emission (I_D) with respect to that of the ZnO nanorods without Pt nanoparticles (I_{D0}).

which suppressed the defect emission of the nanorods. The underlying mechanism of our approach is based on the resonant coupling between the bandgap transition of semiconductor nanorods and the surface plasmon of metal nanoparticles. The suppression of defect emission is due to the surface modification of the sputtered Pt nanoparticles and carrier transfer from the defect level to the Fermi level of Pt nanoparticles. Our unique approach is able to enhance the intensity ratio between the bandgap and defect emission by a factor of up to 10^3 times. Our results should be very useful for manufacturing a wide variety of highly efficient optoelectronic devices such as fluorescence biolabels, light-emitting devices, laser diodes, etc.

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