Selectively enhanced band gap emission in ZnO/Ag$_2$O nanocomposites

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Abstract: A new composite consisting of ZnO nanorods decorated with Ag$_2$O nanoparticles has been synthesized and characterized. It is found that the band gap emission of ZnO nanorods can be greatly enhanced by about 10 times, while the defect emission can be suppressed to the detection limit, simultaneously. The ratio between the band gap and defect emission reaches an enhanced factor of about 600 times. The underlying mechanism is attributed to the combined effects of surface modification, band alignment, as well as charge transfer. Our approach provided here can be extended to many other semiconductors for creating nanocomposites with novel optical properties.

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References and links

1. Introduction

ZnO nanostructures have been widely studied because of their unique optical and piezoelectric properties [1-12]. Especially, the wide band gap of 3.37 eV and the high excitonic binding energy of 60 meV are beneficial for the optoelectronic devices operating at high temperature with excellent stability [1,2]. However, it is well known that a large amount of photoexcited carriers may be trapped by structural defects, such as oxygen vacancies, which leads to poor light emitting efficiency [3-6]. To overcome this obstacle, several methods have been attempted to improve the light emitting efficiency of the optoelectronic devices based on ZnO nanostructures, such as hydrogen doping, annealing, or metal doping [7-12]. In all of these methods, the underlying mechanisms for the improvement were attributed to the passivation of defects by doping atoms, such as H, N, O, or metal atoms, or the carrier transfer from a larger band gap of the coating semiconductor to ZnO nanostructures. In this study, we provide another approach based on newly deviced ZnO/Ag\textsubscript{2}O nanocomposites. By decorating with Ag\textsubscript{2}O nanoparticles, it is found that the band gap emission of ZnO nanorods can be greatly enhanced by about 10 times, and the defect emission can be suppressed to the detection limit, simultaneously. A possible mechanism based on the combined effect of surface modification, band alignment, and charge transfer between Ag\textsubscript{2}O and ZnO nanostructures has been proposed to interpret the giant PL enhancement. Our current study can be extended to many other semiconductors and should be very useful for creating varieties of nanocomposite materials with novel optical properties [13, 14].

2. Experiment

ZnO nanorods studied in this work were prepared by vapor-liquid-solid (VLS) process [1]. 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\textsuperscript{-1} and kept at this temperature for a certain period of time, such as 60 min. After the furnace cooled down, white and grayish-white color products formed on the surface of the sapphire substrate. The Ag\textsubscript{2}O nanoparticles were deposited by the sputtering system (JFC-1600, JEOL), with a current of 20 mA and several different deposition times. The morphology of ZnO nanorods, Ag\textsubscript{2}O nanoparticles and ZnO/Ag\textsubscript{2}O nanocomposites were characterized by scanning electron microscopy (SEM) (JSM6500, JEOL). X-ray diffraction (XRD) pattern was used to identify the structure of the resultant products. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using Jobin Yvon SPEX Fluorolog 3 spectroscope and a 450W Xe lamp was used as the excitation source.
3. Results and discussion

Fig. 1. Scanning electron microscopy images of ZnO nanorods without (a) and with (b) Ag$_2$O nanoparticles.

Figure 1 is the SEM images of ZnO nanorods without (a) and with (b) Ag$_2$O nanoparticles. The ZnO nanorods form a well organized hexagonal shape grown on sapphire (a-plane) with diameters from 90 to 160 nm, and a length of about 2 µm. Figure 1(a) shows that there exists a hemisphere Au catalyst at the top end of ZnO nanorod. In Fig. 1(b), we can clearly see that some Ag$_2$O nanoparticles have been deposited on the surface of ZnO nanorods.

Fig. 2. (a) X-ray diffraction pattern of Ag$_2$O nanoparticles. (b) Photoluminescence and (c) Photoluminescence excitation spectra of Ag$_2$O nanoparticles.

To further characterize the Ag$_2$O material we deposited, Ag$_2$O nanoparticles grown on silicon substrates using the same deposition condition were studied. The composition of the
Ag₂O nanoparticles was examined by XRD measurement. The XRD pattern shown in Fig. 2 (a) confirms the existence of Ag₂O nanoparticles. Figures 2(b) and 2(c) show the PL and PLE spectra of Ag₂O nanoparticles, respectively. The photoluminescence peak at 535 nm corresponds to the band gap of Ag₂O [15], and the photoluminescence excitation spectra monitored at 535 nm exhibits the absorption peak at 460 nm related to the excited state transition of Ag₂O. All these results clearly indicate that the deposited nanoparticles are indeed Ag₂O material.

Figure 3(a) shows the PL spectra of ZnO nanorods and ZnO/Ag₂O nanocomposites with different sputtering times excited by the 325 nm radiation from a 450W Xe lamp. The bare ZnO nanorods exhibit a weak band gap UV emission at 382 nm, and a relatively strong defect emission around 510 nm. Surprisingly, after depositing Ag₂O nanoparticles, a giant enhancement of the band gap emission is observed, while the defect emission is reduced and suppressed to the detection limit. Here, the PL intensity ratio between the band gap and defect emission can be increased by up to 600 times. After the sputtering time exceeds more than 40 seconds, the band gap emission at 382 nm quenches. The variation of the PL intensity ratio of the band gap and defect emission with different sputtering times is shown in Fig. 3(b).

In order to resolve the underlying mechanism for the PL enhancement, first we consider

![Fig. 3. (a) Photoluminescence spectra of ZnO nanorods with and without Ag₂O nanoparticles. (b) Sputtering time dependence of the intensity ratio of UV and defect emission.](image-url)

![Fig. 4. Carrier transfer process in ZnO/Ag₂O composites with and without surface defects in ZnO nanorods.](image-url)
surface modification. As reported previously [3-6], oxygen vacancies localized on ZnO surface are responsible for the defect emission around 510 nm. Similar to other studies [12,16,17], during our deposition process of Ag$_2$O materials, the captured oxygen atoms or Ag$_2$O nanoparticles can interact with surface defects. This behavior will change the defect structures and lead to the passivation of deep defect activity. Therefore, more energetic electrons in the conduction band recombine with the holes in the valence band, thus the band gap emission is enhanced. After sputtering too many Ag$_2$O nanoparticles, the band gap emission could be shadowed by the Ag$_2$O nanoparticles, and the detected PL intensity is quenched. Therefore, surface modification of defect structures seems to be a plausible origin responsible for the observed PL enhancement. However, with a more careful examination of our measurement, it is very difficult to believe that without a full coverage of Ag$_2$O nanoparticles on ZnO nanorod surface, the defect emission can be completely quenched as shown in our experiment. In this respect, in addition to surface modification, we have tried other mechanisms for the enhancement of the band gap emission.

Together with our PL and PLE measurements described above and previous reports [1,2,15], we draw the band alignment as shown in Fig. 4. After the photoexcitation and generation of electron-hole pairs in Ag$_2$O nanoparticles, the excited electrons can transfer to the surface defect states in ZnO nanorods and the excited holes still remain inside Ag$_2$O particles. This spatially separated electrons and holes create an electric field near ZnO and Ag$_2$O interface and cause the band bending as shown in Fig. 4(a). Because of the band bending, the photoexcited electrons in ZnO nanorods are unable to diffuse to the surface and confined in the middle channel of the nanorods. Therefore, the recombination probability of electrons and holes inside ZnO nanorods is increased and leads to the enhancement of the band gap emission. Besides, due to the spatial separation of electrons and holes around the surface defects, the defect emission is suppressed.

![Fig. 5. Photoluminescence spectra of ZnO nanorods grown by CVD process with and without Ag$_2$O nanoparticles.](image)

In our proposed mechanism for the PL enhancement, the existence of surface defects plays a very significant role. One would expect that in the absence of surface defect states, the photoexcited electrons and holes in ZnO nanorods can easily transfer to Ag$_2$O particles due to the band alignment as shown in Fig. 4(b). Under this circumstance, the band gap emission will be quenched after the decoration of Ag$_2$O particles. To confirm this prediction, another ZnO nanorods sample grown by chemical vapor deposition (CVD) process was chosen to repeat all the experiments [18]. This sample contains no defect emission as shown in Fig. 5. It is interesting that the band gap emission quenches immediately after sputtering few Ag$_2$O nanoparticles, which is in good agreement with our prediction. Again, this behavior is
inconsistent with the reduction of defect states due to the effects of surface modification as described above. Thus, it is fairly to conclude that the enhancement of the band gap emission in ZnO nanorods is dominated by the nature of the band alignment in the composite of ZnO nanorods and Ag₂O nanoparticles and the interface band bending arising from charge carrier transfer.

4. Conclusions

In summary, an alternative approach based on the combined effect of surface modification, band alignment, and charge transfer has been provided to improve the light emitting efficiency of ZnO nanorods. By the decoration of Ag₂O nanoparticles, it is found that the band gap emission of ZnO nanorods can be greatly enhanced by about 10 times and the defect emission can be suppressed to the detection limit, simultaneously. The PL intensity ratio between the band gap and defect emission reaches to an enhanced factor of about 600 times. Our approach is believed to be applicable to many other semiconductor materials for the creation of nanocomposites with novel optical properties.

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