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Giant white and blue light emission from Al_2O_3 and ZnO nanocomposites

Yung-Ting Chen, Chung-Liang Cheng and Yang-Fang Chen¹

Department of Physics, National Taiwan University, Taipei 106, Taiwan

E-mail: yfchen@phys.ntu.edu.tw

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Abstract

A new and general approach enabling us to amplify not only the bandgap emission of ZnO nanorods but also the defect emission of Al_2O_3 is proposed. The light intensity of the band edge emission of ZnO nanorods can be improved by as much as 19 times after the decoration of Al_2O_3 layers. Moreover, white light emission arising from Al_2O_3 defects in ZnO/ Al_2O_3 nanostructures also shows a large enhancement factor of 12 times. Our new strategy offers an alternative possibility to create strong white and blue light-emitting devices.

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

1. Introduction

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 [1, 2]. One of the major obstacles to be overcome for the application of ZnO nanostructures in optoelectronic devices is to reduce the defect loss and enhance the bandgap emission simultaneously. Numerous studies have been conducted to obtain a higher efficiency of light emission from ZnO nanostructures [3–6]. Recently, we have reported that, in the nanocomposite consisting of SnO and ZnO, the transfer of electrons and holes from SnO nanoparticles to ZnO nanorods results in the enhancement of the band edge emission of ZnO nanorods, and the defect emission can be suppressed due to surface modification of ZnO nanorods [4]. Here, we explore the possibility for the creation of high efficiency solid state emitters using Al_2O_3 and ZnO nanocomposites. The photoluminescent properties of Al_2O_3 have been investigated in past decades [8–14]. It is found that oxygen ion vacancies play an important role for the emission arising from Al_2O_3 . Quite interestingly, our result demonstrates that not only the bandgap emission of ZnO nanorods in the ultraviolet region but also the defect emission of Al_2O_3 in the visible region can be greatly enhanced. The result shown here indicates that it is

possible to fabricate white light-emitting devices with the help of Al_2O_3 /ZnO nanocomposites.

2. Experimental details

In this experiment, ZnO nanorods were prepared by a vapor-liquid-solid process. A mixture of high purity ZnO and carbon powders (the molar ratio is 1:1) were used for the growth. The mixed powders were placed on an alumina boat and the boat was placed at the center of a quartz tube. At the same time, the gold-coated sapphire was placed on the same boat at a distance away from the powders of about 3 cm. Finally, we put the quartz tube into the heater. The tube was heated to 980 °C at a rate of 40 °C min⁻¹. The reaction was kept for about 60 min. After the furnace was cooled down, white and grayish-white color products formed on the surface of the sapphire substrate [5].

Al_2O_3 was synthesized by a sol-gel process presented by Masalski *et al* [7]. Briefly, the typical synthesis procedure is as follows. Aluminum isopropoxide ($\text{Al}(\text{OC}_3\text{H}_7)_3$) powder was added under constant stirring to a boiling solution of 450 ml DI water and 1 ml HNO_3 ($d = 1.38$). The hydrolysis procedure follows the reaction [7]: $2\text{Al}[(\text{CH}_3)_2\text{CHO}]_3 + (3 + n)\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O} + 6(\text{CH}_3)_2\text{CHOH}$. When the mixture was evaporated down to 225 ml, 4 ml HNO_3 was added in order to clear the solution. When cooling down to room temperature, a translucent Al_2O_3 gel was obtained. Then the Al_2O_3 gel was coated onto ZnO nanorods by using a spin coating system.

The morphology and component of ZnO nanorods were characterized by scanning electron microscopy (SEM) (JSM

¹ Author to whom any correspondence should be addressed.

Figure 1. Scanning electron microscope images of (a) pure ZnO nanorods at a tilt angle of 20°, (b) the cross section of pure ZnO nanorods and (c) the cross section of the $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites.

6500, JEOL). Photoluminescence (PL) spectra were obtained with a SPEX Fluorolog-2 instrument equipped with a double-grating monochromator and a R928 photomultiplier tube. The excitation source was provided by a 450 W Xe lamp with a wavelength of 325 nm at room temperature.

3. Results and discussion

Figure 1(a) shows the SEM image of ZnO nanorods at a tilt angle of 20°. The ZnO nanorods are well aligned and have an average diameter of 50 nm and a length of about 2.9 μm . Figures 1(b) and (c) depict, respectively, the SEM images of the cross sections of pure ZnO nanorods and the $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites. It is obvious that a thick layer of Al_2O_3 with an average thickness of about 100 nm has been covered on ZnO nanorods.

Figure 2(a) shows the room-temperature PL spectra of pure ZnO nanorods, Al_2O_3 gel coated on an Si substrate and the $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites after annealing at various temperatures in Ar ambience for two hours. For pure ZnO nanorods, the peak at 380 nm can be attributed to the band edge emission, and the broad band centered around 500 nm has been assigned to the transition related to oxygen vacancies [5]. For Al_2O_3 gel alone, it exhibits a rather weak emission around 400 nm, and it does not have a significant change in the intensity under the various conditions of annealing. In contrast, under various annealing temperatures, Al_2O_3 gel-coated ZnO nanorods emit strong blue light or white light, which can be observed even with the naked eye. Examining figure 2, we further find that, at 380 nm emission, the light intensity of Al_2O_3 gel-coated ZnO nanorods after annealing at 600°C is as much as 19 times larger than that of pure ZnO nanorods.

Figure 2(b) shows the room-temperature PL spectra of pure ZnO nanorods before and after annealing at 500 and 600°C in Ar ambience for two hours. The result shows, under thermal treatment, that the band edge emission of ZnO nanorods decreases and the defect emission of ZnO

Figure 2. (a) Room-temperature PL spectra of pure ZnO nanorods, Al_2O_3 gel coated on an Si substrate and $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites after annealing at various temperatures in Ar ambience for two hours. (b) Room-temperature PL spectra of pure ZnO nanorods before and after annealing at 500 and 600°C in Ar ambience for two hours. (c) Room-temperature PL spectrum of pure ZnO nanorods and the peak fitting for a room-temperature PL spectrum of $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites after annealing at 600°C.

nanorods increases; however, the change is relatively small. As a result, it eliminates the possibility that the annealing temperature and annealing time in Ar may be one of the effects that change the light intensity from ZnO nanorods in the $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites. Besides, according to the

Figure 3. Room-temperature PL spectra of pure ZnO nanorods and the $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites after annealing at 300 °C in Ar ambience for two hours.

peak fitting as shown in figure 2(c), it clearly indicates that the ZnO defect emission at around 500 nm decreases and its band edge emission at around 380 nm increases after the decoration of the Al_2O_3 layer and thermal treatment, and the fitting peaks centered at 400 and 484 nm can be attributed to the surface defect emission from the Al_2O_3 layer [12]. The above result probably indicates that the interaction between Al_2O_3 gel and ZnO nanorods significantly affects the photoluminescent intensity of $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites. Here, we propose a possible underlying mechanism to describe the observed behavior. After annealing from 300 to 600 °C, the structure of the Al_2O_3 layer changes from boehmite (AlOOH) to $\gamma\text{-Al}_2\text{O}_3$ [12]. The dehydration causes oxygen atoms be removed from the surface of boehmite [15, 16] and occupy the oxygen vacancies on the surface of ZnO nanorods. Therefore, the defect emission at around 500 nm arising from oxygen vacancies of ZnO nanorods decreases, and the band edge emission increases. Besides, according to our proposed mechanism, the enhanced emission for oxygen vacancies in Al_2O_3 follows naturally because oxygen atoms escape away from the Al_2O_3 film.

In order to confirm that the mechanism of the enhanced emission from $\text{Al}_2\text{O}_3/\text{ZnO}$ nanocomposites is indeed due to the movement of oxygen atoms from Al_2O_3 to the ZnO surface, the other two samples have been measured. The first sample was ZnO nanorods with negligible defects, which were grown by the chemical vapor deposition (CVD) approach [17]. A detailed procedure of the CVD process has been described elsewhere [17]. Its room-temperature PL spectra before and after being coated with Al_2O_3 gel and annealed at 300 °C were shown in figure 3. The figure reveals that the bandgap emission of ZnO nanorods is largely suppressed and the emission from the Al_2O_3 film is rather weak, which is quite different from the spectra for ZnO nanorods with a large amount of oxygen vacancies. This result can be easily understood, because without oxygen vacancies on ZnO nanorods, oxygen atoms cannot move from Al_2O_3 to ZnO. Without the passivation of surface defects, the enhancement of the band edge emission of ZnO nanorods does not occur. Instead, the defect levels in the Al_2O_3 layer can trap electron–hole pairs generated in ZnO

Figure 4. Room-temperature PL spectra of pure SnO_2 nanorods and the $\text{Al}_2\text{O}_3/\text{SnO}_2$ nanocomposites after annealing at various temperatures in Ar ambience for two hours.

nanorods, and it causes the decrease of the band edge emission from ZnO nanorods. This situation is very different from the case of ZnO nanorods with a large amount of surface defects. Therefore, the results shown here do support our proposed mechanism.

The second sample we studied was SnO_2 nanorods prepared by the thermal evaporation method [18] and its room-temperature PL spectra before and after annealing at various temperatures were shown in figure 4. It is found that, at 300 °C, the defect emission centered at 584 nm from SnO_2 is reduced and the defect emission of Al_2O_3 film is notably increased. This result can also be explained quite well in terms of our proposed mechanism, in which oxygen atoms can move from the Al_2O_3 film to the oxygen vacancies located on the SnO_2 surface. Therefore, the defect emission from SnO_2 is reduced, and the emission from oxygen vacancies in Al_2O_3 is enhanced. It is worth noting that the blue emission arising from Al_2O_3 defects studied here shows a rather strong intensity at room temperature and can be clearly observed with the naked eye. Thus, our result demonstrates that our proposed principle does work well and we can fabricate white and blue light-emitting devices based on $\text{Al}_2\text{O}_3/\text{oxide}$ semiconductor nanocomposites.

4. Conclusion

In summary, we have presented an effective approach for simultaneously amplifying light intensity of the bandgap emission of ZnO nanorods in the ultraviolet region and the defect emission of Al_2O_3 in the visible region. The underlying mechanism responsible for the enhancement is attributed to the movement of oxygen atoms in the Al_2O_3 film to oxygen vacancies on the surface of ZnO nanorods. It is believed that our approach should be very useful in the design of many other nanomaterial composites for creating a wide variety of high efficiency optoelectronic devices, such as fluorescence biolabels, light emitters, laser diodes, etc.

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