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Suppression of Green Emission in ZnO Nanorods—A Discussion on Surface and Interior Structural Quality Manipulation

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Two kinds of ZnO nanorods were synthesized using thermal evaporation and solvothermal methods. Both of the as-prepared samples exhibit strong green luminescence, which is commonly attributed to the surface defect emission of the nanostructure due to its large surface-to-volume ratio. However, we found surface passivation of these ZnO nanorods by a thin SiO₂ layer failed to improve the band edge emission and reduce the green emission significantly. On the other hand, we found that introducing Ga to the ZnO nanorods during the thermal evaporation growth would significantly depress the green emission. The experimental results suggested that the interior structure quality of the ZnO nanorods is sensitive to the growth techniques and conditions, and surface defects of ZnO are not necessarily responsible for the green emission observed from these nanorods.

Introduction

ZnO has gained substantial interest in the research community for many decades as a multifunctional semiconductor material.¹ It has been studied as a candidate for transparent electrodes, piezoelectric transducers, viable ultraviolet laser material, phosphors, etc.² The successful fabrication of ZnO nanostructures in recent years^{3–5} and its possible development with the continuous advancement of nanotechnology further fueled the research on this material. In particular, the optical property of ZnO, including its thin film, powder, and low-dimensional nanostructure counterparts, is one of the research focus.^{6–9}

A typical luminescence spectrum of ZnO consists of an ultraviolet excitonic emission peak and emission peak(s) in the visible range due to its deep level defects. The reported visible emissions from different ZnO samples include red, orange, yellow, green, and blue luminescence.^{10,11} Among them, the green emission is the most commonly observed, and the origin for such a peak remains as the most controversial.^{9,12} Multiple origins of this green luminescence (GL) band have been proposed in ZnO samples prepared by different methods. It has been suggested that the GL band with a characteristic fine structure is most likely related to the copper impurities, whereas the featureless GL band could relate to native point defects, such as oxygen vacancy (V_O) and/or Zn vacancy (V_{Zn}).¹ Bulk single crystals and phosphor powders are more likely to exhibit extrinsic impurity related emission, whereas nanostructures and thin films to intrinsic defects.^{1,8,9}

A number of studies have suggested that the green emission originates from the surface defects, particularly when one deals with ZnO nanostructures,^{2,9,11} due to their large surface-to-volume ratio. In this regard, one would expect that surface passivation, especially by large band gap materials (larger than

that of ZnO), would enhance the ZnO band edge emission and depress the green emission. Nevertheless, our experimental observation does not agree with this general principle; that is, significantly improved band edge emission and depression of the green emission are not observed when the surface of the ZnO nanorods is passivated with a thin layer of SiO₂. Instead, we found that the ratio of the band edge to green emission of ZnO samples is sensitive to their preparation method, suggesting that the interior structural quality of the ZnO nanorods plays an important role in determining their luminescence behavior.

Experimental Section

ZnO nanorods used in this experiment were prepared by both a thermal evaporation method and a solvothermal method. For the evaporation approach, a high-temperature vacuum tube furnace is employed, whose set up can be found in elsewhere.¹³ A small quartz tube (12 mm × 20 cm) was located in the center of the big vacuum tube (40 mm × 70 cm). A mixed powder of ZnO and C was loaded into the closed end of the small tube (at the center of the tube furnace) as source material, and a piece of Si wafer was placed at the open end of that tube (upstream of the tube furnace) for sample collection. The big vacuum tube was then sealed and pumped up to 3.5×10^{-2} Torr. Pure Ar (80 sccm) was introduced into the system as the carrier gas. Total pressure in the system was kept at 300 mbar for the whole process. The furnace was then heated up to 1100 °C and kept at the same temperature for 1 h. Pure O₂ (20 sccm) was introduced into the system after the temperature reached 1100 °C for 5 min. Ga-doped ZnO nanorods were also prepared using the same synthesis setup and conditions, while Ga₂O₃ powder (with a molar ratio of 1/20 of ZnO) was added into the source material.

The ZnO nanorods synthesized by a solvothermal method were intentionally grown on a heat-resistant substrate copper due to the later high-temperature requirement during the surface layer growth process. First, a thin Zn layer was plated on a Cu foil using an acidic zinc chloride solution. The foil was then added to a mixed aqueous solution of NaOH and H₂O₂, which

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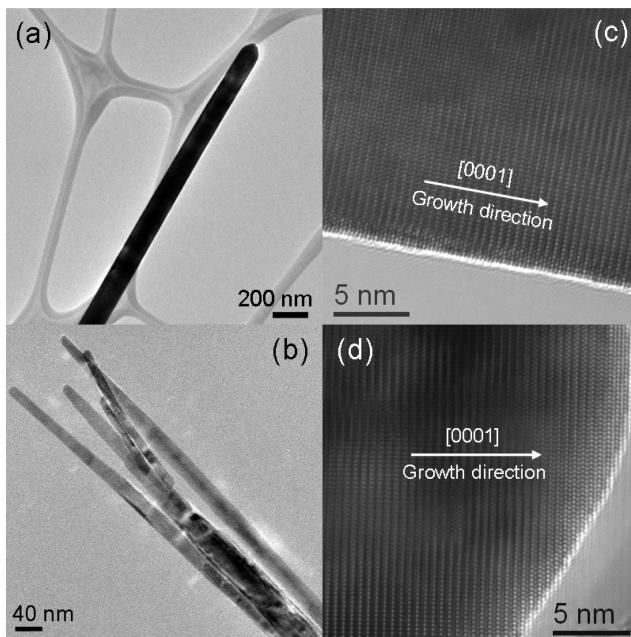


Figure 1. (a, b) Low-magnification TEM images showing the general morphology of the as-synthesized ZnO nanorods by thermal evaporation and a solvothermal method, respectively. (c, d) High-resolution TEM images taken from ZnO nanorods shown in (a, b), respectively. Both of them show single-crystal ZnO with an hexagonal lattice.

is filled in a stainless steel Teflon-lined autoclave. After the autoclave was sealed, it was kept at a constant temperature in an oven for several hours until the Zn layer was exhausted. At last, the foil was taken out from the solution when the system returns to room temperature, rinsed with distilled water, and dried in air.

The SiO₂ layer was deposited on the ZnO nanorods in the same high-temperature vacuum tube furnace by vapor transport deposition. SiO powder was placed at the center of the tube and thermal evaporated at 1000 °C. The ZnO nanorods were placed at the downstream of the tube, with a temperature at an ~680 to 650 °C zone when the center temperature reaches 1000 °C. Initially, pure Ar was used as carrier gas and the total pressure in the system was kept as 300 mbar. After 30 min evaporation and deposition, the carrier gas was switched to pure O₂ and the total pressure in the system was kept slightly larger than 1 atm for 2 h.

A field emission scanning electron microscope (QF 400) was used to examine the general morphology of the specimens. A Tecnai-F20 FEGTEM equipped with an energy-dispersive X-ray spectroscope (EDX) and an electron energy loss spectrometer (EELS) was used to investigate the microstructure and the composition of the samples. Cathodoluminescence (CL) measurements of the samples were performed at room temperature using a MonoCL system (Oxford Instrument).

Results

Figure 1a,b shows the low-magnification TEM images taken from the as-synthesized specimens by an evaporation and a solvothermal method, respectively. The nanorods prepared by the evaporation method have an average diameter of ~150 nm, whereas those prepared by the solvothermal method have a smaller average diameter, ~30 nm. All nanorods have the hexagonal structure, which is consistent with the XRD taken from them (Figure 2). These nanorods grow along the ZnO [0001] crystalline direction (Figure 1c,d), and their outer surface appears to be smooth.

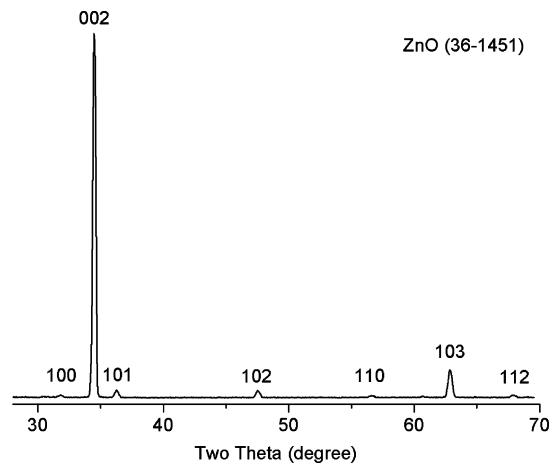


Figure 2. Typical XRD spectrum taken from the as-prepared ZnO nanorods.

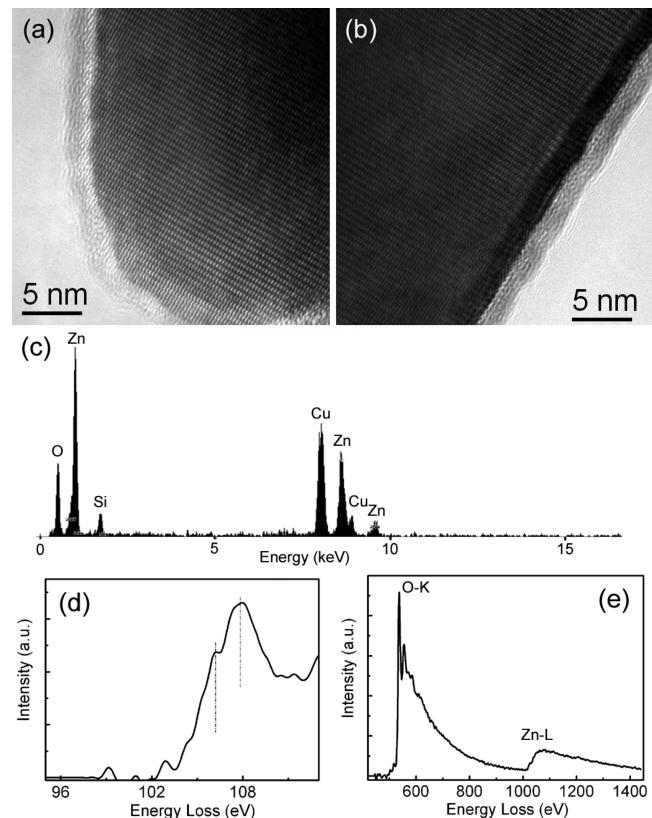


Figure 3. (a, b) High-resolution TEM images taken from the ZnO nanorod with an amorphous SiO₂ surface layer. (c) EDX spectra taken by focusing the electron beam on the surface region of the sample, showing the signal of Si and O. (d) EELS taken by locating the electron beam at the surface layer of the ZnO nanorod; the line shape of the Si L-edge is characteristic of SiO₂. (e) EELS taken by locating the electron beam at the interior of the ZnO nanorod. The O K-edge and Zn L-edge can be clearly observed.

After depositing the SiO₂ surface layer, the morphologies of both specimens are not destroyed. Figure 3a,b shows typical high-resolution TEM images taken from the surface-modified nanorods. It can be seen that an ~2 nm thick amorphous layer was uniformly grown on the surface of the single-crystalline nanorod. EDX analysis (Figure 3c), which was performed by focusing an ~2 nm electron beam probe on the amorphous layer, reveals that the thin layer contains Si and O only. Electron energy loss spectra were taken by focusing the electron beam on the amorphous surface layer and the core of the same

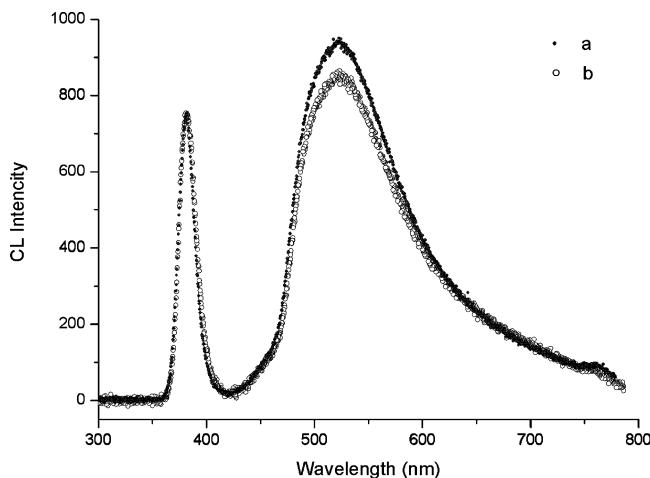


Figure 4. Room-temperature CL spectra taken from (a) as-synthesized ZnO nanorods and (b) ZnO nanorods with a SiO₂ surface layer. The nanorods were synthesized by a thermal evaporation method. The spectra were normalized using the ZnO band edge emission.

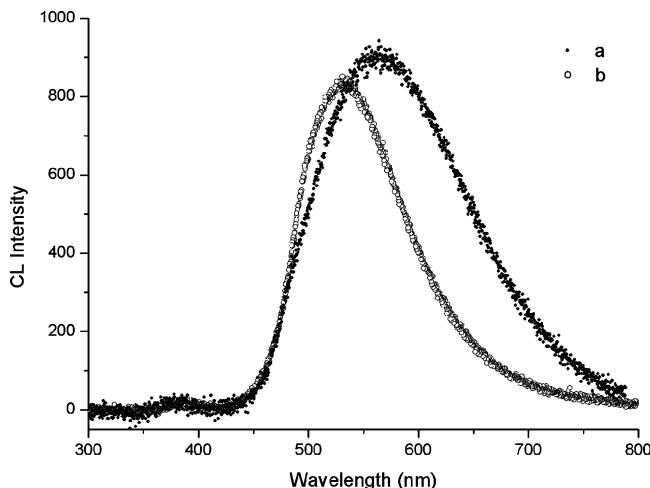


Figure 5. Room-temperature CL spectra taken from (a) as-synthesized ZnO nanorods and (b) ZnO nanorods with a SiO₂ surface layer. The nanorods were synthesized by a solvothermal method. The spectra were normalized using the ZnO band edge emission.

nanorod. In Figure 3d, a signature of the Si L-edge fine structure as in SiO₂ (Si⁴⁺)^{14,15} is observed, with an onset at 106 eV and a later peak centered at 108 eV, suggesting that the amorphous surface layer is composed of SiO₂. When the electron probe is moved to the core region of the specimen, energy loss signals from the O K-edge and the Zn L-edge can also be observed (Figure 3e), which is consistent with the existence of the ZnO nanorod core.¹⁶ Over the hundreds of nanorods examined, the surfaces of all of them have been uniformly covered with a thin layer of SiO₂.

Typical room-temperature cathodoluminescence spectra of nanorods prepared by different methods are shown in Figures 4 and 5. Besides the band edge emission at ~385 nm, the as-synthesized nanorods by evaporation show a broad green emission with an intensity maximum at ~530 nm (Figure 4, spectrum a). When the surface of these nanorods was deposited by a thin layer of SiO₂, the green emission was only slightly depressed without any obvious change on the peak line shape (Figure 4, spectrum b). The major peak features in the spectra of the solvothermal ZnO nanorods and their evolution after the surface modification are rather similar to those by evaporation methods, that is, band edge emission at ~385 nm and a green

emission, and the green emission is slightly weakened when the surface of the solvothermal ZnO is covered with SiO₂. Nevertheless, one shall notice that a much smaller band edge-to-green emission ratio exists in the solvothermal nanorods, as compared with that of the evaporation ones. In addition, the green emission bands are broader in the solvothermal nanorods, with a peak maximum shifting to 570 nm (Figure 5, spectrum a). When the nanorod surface is deposited with a thin layer of SiO₂, obvious narrowing of the defect emission in the visible range is observed, with its peak center blue shifted to ~530 nm, which is the same as that of the evaporated ZnO nanorods (Figure 5, spectrum b).

Discussion

We first discuss the possible origin of the green emission in the ZnO nanorods. In the literature, Cu impurity in ZnO has been reported to induce a green luminescence.^{17–19} However, a Cu signal was not found in our specimen, when analyzed using secondary-ion mass spectroscopy (SIMS). With the measurement sensitivity in the range of several parts per million and below, such a result suggests the absence of the Cu impurity in our sample. In addition, the emission originated from the interstitial Cu has a maximum at ~510 nm,^{17–19} being different from that observed in our samples (~530 nm). The other common explanation for the green emission is the intrinsic defects involving O and Zn,^{8,12} which is likely the explanation for the green emission in our specimen. For nanorods synthesized by the solvothermal method, the much broader peak in the visible range indicates contribution from not only the green emission but also yellow and orange luminescence as well. The yellow and orange emissions (~570 nm) were commonly assigned to –OH defects, which is easily introduced, in particular, at the surface of the nanorods, during the solvothermal process.

When the surfaces of the as-synthesized nanorods are deposited with a thin layer of SiO₂, the reduction on green emission indeed suggests that surface passivation would suppress the surface defect emission, and as a result, the band edge-to-defect emission ratio is increased. This is usually explained as termination of dangling bonds on the ZnO nanorod surface²⁰ by a layer of larger band gap material (SiO₂ in the present case). As a matter of fact, the defect emission center shifting from ~570 to ~530 nm observed in the surface-passivated solvothermal ZnO nanorods (by SiO₂) suggests a change in the dominant defect type after the surface SiO₂ layer is grown on the ZnO nanorods. This indicates that the ZnO surface has been modified by the SiO₂ deposition; one shall expect removal of the surface –OH group during the surface SiO₂ growth at elevated temperatures. Nevertheless, one shall notice that such surface modification fails to significantly reduce the green emission centered at ~530 nm, which results suggested that the deep level defects contributing to the green emission may not only be limited on the nanorod surface but also in the interior of the ZnO nanorods.

In this regard, we have attempted introducing the Ga during the ZnO nanorod growth (using a thermal evaporation method), as substitutional Ga in the ZnO is known to a form shallow donor level, which increases the free electron density and thus compensates the O vacancy defects,²¹ contributing to the suppression of the green emission that originates from the O vacancy related defects. The specimen maintains the nanorod morphology, with a similar average diameter as that of its undoped counterpart. Each nanorod also has the hexagonal structure and grows along the crystalline [0001] direction. A

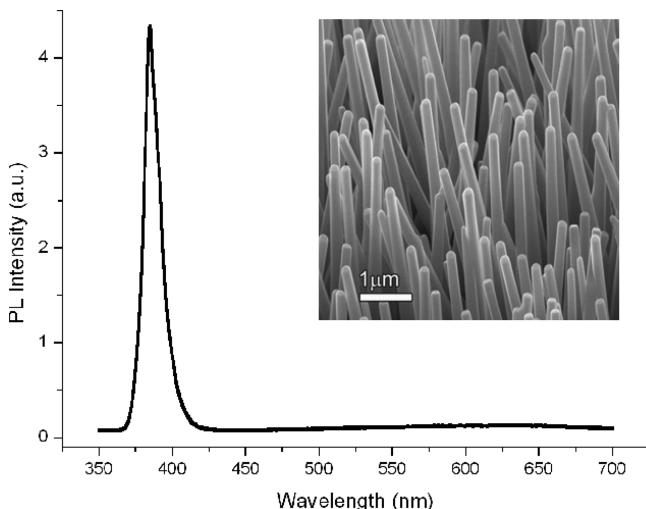


Figure 6. Room-temperature PL spectra taken from Ga-doped ZnO nanorods, which are fabricated by a thermal evaporation method. A side-view SEM image showing the aligned configuration of the nanorods can be found in the inset.

successful doping was confirmed by both SIMS measurements and electrical measurement on single nanorods; that is, the electrical resistivity of the sample is reduced to $10^{-3} \Omega \cdot \text{cm}$, being 2 orders of magnitude lower than that of the unintentionally doped ZnO ($10^{-1} \Omega \cdot \text{cm}$).²² Figure 6 shows the photoluminescence spectrum taken from Ga-doped ZnO nanorods, and one can see that little green emission around 530 nm exists after the Ga doping.

Conclusion

We have prepared two types of ZnO nanorods samples using thermal evaporation and solvothermal methods. Both of the as-prepared specimens exhibit strong green luminescence, which is commonly attributed to the surface defect emission of the nanostructure due to its large surface-to-volume ratio. We have found passivating the ZnO nanorod surface with a thin SiO₂ layer fails to significantly depress the green emission in both types of ZnO samples, whereas introducing Ga to the ZnO nanorods during the thermal evaporation growth serves as an effective means for the green emission suppression. These experimental results suggest that surface defects, although they contribute to, may not be mainly responsible for the intense

green emission observed in the ZnO nanorods. The interior structure quality, which is sensitive to the preparation method and conditions, plays important roles in determining the luminescence behavior of the ZnO nanostructures.

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