Ultraviolet Electroluminescence from ZnS@ZnO Core–Shell Nanowires/p-GaN Introduced by Exciton Localization

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Supporting Information

ABSTRACT: We investigate the electroluminescence (EL) from light emitting diodes (LEDs) of ZnO nanowires/p-GaN structure and ZnS@ZnO core–shell nanowires/p-GaN structure. With the increase of forward bias, the emission peak of ZnO nanowires/p-GaN structure heterojunction shows a blue-shift, while the ZnS@ZnO core–shell nanowires/p-GaN structure demonstrates a changing EL emission; the ultraviolet (UV) emission at 378 nm can be observed. This discrepancy is related to the localized states introduced by ZnS particles, which results in a different carrier recombination process near the interfaces of the heterojunction. The localized states capture the carriers in ZnO nanowires and convert them to localized excitons under high forward bias. A strong UV emission due to localized excitons can be observed. Our results indicated that utilizing localized excitons should be a new route toward ZnO-based ultraviolet LEDs with high efficiency.

KEYWORDS: ZnO, core–shell nanowires, localized excitons, electroluminescence, gan, heterojunction

1. INTRODUCTION

Owing to its wide band gap (3.37 eV) and high exciton binding energy (60 meV), ZnO has been considered to be the most important optoelectronic semiconductor material, especially for the next generation solid-state lighting sources. However, the realization of stable and reproducible p-ZnO is still challenging, which hinders the further development of ZnO-based homogeneous junction devices. Therefore, the ZnO-based heterojunction has only gradually become an important device structure.

Because of the similarity of crystallographic and electronic properties between ZnO and GaN, the ZnO/p-GaN heterojunction is employed as one of the most effective ways to realize blue/ultraviolet (UV) electroluminescence (EL) emission. However, the recombination of electrons and holes near the interface, due to higher concentration and mobility of electrons in ZnO than that of holes in p-GaN, results in the EL emission being out of the UV region (in the blue region). Therefore, developing a structure of ZnO heterojunction which can achieve the recombination of electrons and holes at ZnO to realize UV emission has received much attention.

Currently, various ZnO/p-GaN heterojunction structures have been proposed, and the method of inserting layers between ZnO and GaN are recognized as an effective way to control the carrier transport and the emission wavelengths. However, the intermediate layer has limited the carrier transportation and leads to low light emitting efficiency. Because of the gain of advanced physical and chemical properties, the integration of ZnO nanostructures (nanowires or quantum dots) with GaN could be a feasible approach to obtain light-emitting diodes (LEDs) with high performance. Several kinds of low-dimensional nanostructures have been studied extensively; however, it is known that the optoelectronic properties of these devices are greatly influenced by the surface properties of ZnO nanostructures. Thus, various approaches such as quantum dots sensitization and the introduction of localized surface plasmon or localized excitons have been adopted to optimize the performance of ZnO nanostructures.

Herein, we propose the ZnS@ZnO core–shell nanowires/p-GaN structure heterojunctions. The strategy of using a core–shell structure not only allows the efficient use of individual ZnO nanowires but also enhances the charge carrier recombination by localized excitons. It is known that ZnS@ZnO core–shell structures exhibit more excellent optoelectronic properties. Modified by a ZnS coating, surface states of ZnO nanowires can be effectively suppressed. Additionally, the
introduced localized excitons could greatly improve luminescence properties of ZnO nanowires, which play a significant role for UV emission.\textsuperscript{27,30,31} In this paper, we shall compare ZnO nanowires/p-GaN structure and ZnO/ZnS core−shell nanowires/p-GaN structure heterojunctions. The morphology and optical properties of the ZnO nanowire with and without ZnS coating have been investigated. For the EL measurement, carrier transport process and the physical mechanism shall be discussed in detail. Finally, pure UV EL located at 378 nm has been achieved, and it was ascribed to the excitons localization. Our approach provides an alternative way to realize the UV emission from ZnO nanomaterials, which is simple, effective, and accessible for other material systems.

2. EXPERIMENTAL SECTION

Synthesis of ZnO Nanowires/p-GaN Structure. First, 0.01 M zinc acetate and 0.01 M hexamethylenetetramine were dissolved in aqueous solution, then the mixed solution was transferred to a Teflon-lined stainless autoclave of 50 mL capacity. Second, p-GaN was put into the solution. The tank was held in an electric oven at 95 °C for 8 h. After the reaction, the sample was washed by deionized water and dried in air at 60 °C for several hours.\textsuperscript{22}

Synthesis of ZnS@ZnO Core−Shell Nanowires/p-GaN Structure. The ZnS@ZnO core−shell nanowires/p-GaN sample was synthesized by chemical bath deposition (CBD). The as-grown ZnO nanowires/p-GaN sample was immersed in 0.16 mol/L sodium sulfide and 0.16 mol/L zinc nitrate mixed solution at a temperature of 60 °C for 2 h, respectively. After the reaction, the sample was also washed by deionized water and dried in air at 60 °C for several hours.

Preparation ZnO Heterojunction. ZnO nanowires and ZnS@ZnO core−shell nanowires were used as n-type materials, while the p-GaN was used as p-type material. To Ohmic contacts, indium tin oxide (ITO) and Ni−Au/In electrode were sputtered on ZnO and GaN, respectively.

Measurements Conditions. A Hitachi-4800 field emission scanning electron microscope (FESEM) and energy-dispersive X-ray spectroscopy (EDS, GENE SIS 2000 XMS 60S, EDAX, Inc.) attached to the SEM and X-ray diffraction (XRD) were used to characterize the morphology and chemical composition of the samples. A He−Cd laser with line of 325 nm was used as the excitation source to perform PL measurements. EL measurements were performed by a fluorescence meter (F4500 Hitachi). The current−voltage (I−V) curve was measured by a semiconductor parameter analyzer with a sensitivity of 0.1 pA.

3. RESULTS AND DISCUSSION

Figure 1a and Figure 1b show the morphology characterization of ZnO and ZnS@ZnO core−shell nanowires, respectively. It can be seen that both nanowires samples were of the well-defined hexagonal shape. The insets of Figure 1a and Figure 1b show that the diameter of nanowires was estimated to be about 100 nm. Because of the growth of outer ZnS layer, the surface of the core−shell nanowires became rough, and the diameter slightly increased. In addition, ZnS particles with a diameter of about 5 nm can be clearly observed in the TEM images, as shown in the inset of Figure 1c. On the basis of our previous research,\textsuperscript{22} it is noted that the localized states can form at the interface of ZnO nanowires and ZnS particles, which could prevent excitons generated in ZnO diffusing to nonradiative recombination centers.\textsuperscript{21,33} From our photoluminescence (PL) measurement, ZnS@ZnO nanowires exhibited an enhanced UV emission located at 377 nm caused by localized excitons, which was about 4 times higher than the ZnO nanowires (as shown in Figure 1c). Meanwhile, the intensity of defect emission was depressed because of surface passivation.\textsuperscript{34}

Figure 2a and Figure 2b show the EL spectra of the devices under forward bias from 1.5 to 10 V, while the insets are the schematic diagrams and relationship between the integrated EL intensity and voltage of two heterojunctions. For ZnO nanowires/p-GaN, the emission peak at about 430 nm was observed. Similar emission has been detected for ZnS@ZnO core−shell nanowires/p-GaN at lower forward bias. However, at higher forward bias, besides the emission at 430 nm, a new emission at 378 nm appeared. Voltage-dependence of integrated EL intensity of the samples are shown in the insets of Figure 2a and Figure 2b. Increasing the forward bias resulted in an increase of integrated EL intensity of the two devices between 350 and 700 nm. However, the increasing trends of integrated EL intensity were still differences, especially at higher forward bias. In addition, the two structures exhibited different I−V curves as shown in Figure S1. Therefore, we speculated that the EL emission mechanism might be different, especially under higher voltage, and localized excitons caused by ZnS particles might be the origin of the unusual EL emission.

To investigate the emission mechanism of the two structures, EL spectra have been analyzed in detail. The EL spectra can be divided into two parts: Part I (voltage from 1.5 to 4 V) and Part II (voltage from 9 to 10 V). First, we focused on the Part I EL spectra as shown in Figure 3 and Figure 4. Figure 3a shows the EL spectra of ZnO nanowires/p-GaN structure under lower forward bias. With the increase of voltage, a clear blue-shift of the emission from 448 to 432 nm was observed. Moreover, the full width at half-maximum (fwhm) of the peak became narrower. From the band alignment of ZnO/GaN, it is known that the energy barrier ΔE with electrons is around 0.15 eV,\textsuperscript{13,35} while the energy barrier ΔE with holes is around 0.13 eV.\textsuperscript{13,35} Therefore, electrons and holes will recombine in GaN, and the EL emission originated from GaN can be observed.\textsuperscript{16,36} As plotted in Figure 3b, the EL spectra could be well-fitted by two individual Gaussian peaks, which resulted in P1 emission at 430 nm and P2 emission at 460 nm. The peaks were attributed to the transitions from donor level E_D in ZnO to the acceptor
level $E_A$ in GaN (430 nm) and defect emission in GaN (460 nm) based on the previous reports. With the increase of voltage, more and more electrons transferred into GaN, and the intensity of P1 and P2 emissions increased. However, the intensity of P2 emission increases slowly because the saturation of defect levels, and thus the ratio of $P1/P2$ increased gradually. This means electrons in ZnO that transferred into the acceptor level of GaN was dominant, which could also reflect the trend of transitions of electrons as shown in Figure 3c.

For ZnS@ZnO core−shell nanowires/p-GaN, besides a weaker intensity, the shift of peak position and the change of fwhm were almost the same as ZnO nanowires/p-GaN structure (shown in Figure 4a and inset). The EL emission could also be divided into P1 emission and P2 emission peaks by the Gaussian analyses, and the ratio of $P1/P2$ increased as well (Figure 4b and Figure 4c). Therefore, for the two structures under low forward bias, it is concluded that the carriers’ recombination mechanisms are the same, in other words, electrons from ZnO transferred and recombined with holes in GaN. However, due to the existence of localized states in the ZnO/ZnS interface, parts of the generated electrons would convert into localized excitons. So under the same forward bias, the free electrons in ZnS@ZnO core−shell nanowires would be less than ZnO nanowires, which means that the recombination of electrons and holes of p-GaN was suppressed.

For Part II EL spectra, Figure 5a and Figure 5b present the EL emission of the samples under forward bias of 10 V. For the ZnO nanowires/p-GaN heterojunction, the EL emission located at the same position around 430 nm. For the ZnS@ZnO core−shell nanowires/p-GaN structure, UV emission at 378 nm has been observed. As shown in Figure S2, emission peak $P3$ (402 nm) and $P4$ (378 nm) can be deduced with Gaussian
analyses. \( P_3 \) emission was caused by the transitions from the conduction band edge of ZnO to the acceptor level of GaN,\(^{13,19} \) while the \( P_4 \) emission should be the EL emission from ZnO. It can be seen that the ratio of \( P_3/P_1 \) of the two structures was different. For ZnO nanowires/p-GaN structure, this ratio increase indicated that the recombination zone moved from the GaN to the interface of heterojunction. But for ZnS@ZnO core–shell nanowires/p-GaN structure, the increase of \( P_3/P_1 \) was not obvious. On the basis of the existence of \( P_4 \) emission, we concluded that the recombination zone kept moving from the interface to the ZnO nanorods.\(^{35} \)

In Figure 5c and Figure 5d, the schematic diagrams of carrier recombination and energy band schematic diagrams were plotted to explain the carrier transition processes. For the ZnO nanowires/p-GaN structure, the electrons possess a high probability to transit from the side of ZnO to p-GaN, which results in recombination and EL emission of GaN. This process depends on the forward bias. Under higher forward bias, more electrons would be transported into GaN, the blue shift phenomenon and a competitive relationship of \( P_1, P_2, \) and \( P_3 \) could be observed (from the ratio of \( P_1/P_2 \) and \( P_3/P_1 \)). For the ZnS@ZnO core–shell nanowires/p-GaN structure, localized states introduced by ZnS coating would confine parts of free electrons generated in ZnO nanowires. The other electrons in ZnS@ZnO core–shell nanowires could still transit into GaN, and \( P_0, P_2, \) and \( P_3 \) emissions still existed. In previously works, it was shown that ZnO had higher emission efficiency in localized states.\(^{32,37} \) Under high forward bias, such as 9 and 10 V, the holes in GaN could transfer into the localized states of ZnO because of the high internal electric field and recombine with the captured electrons, which leads to the \( P_4 \) emission located at 378 nm. All the processes are presented in Figure 5. Utilizing localized excitons, we have achieved the pure UV emission from ZnO/GaN heterojunction.

### 4. CONCLUSIONS

We have synthesized ZnO and ZnS@ZnO core–shell nanowires. The latter had perfect crystal quality and enhanced UV emission because of localized excitons introduced by ZnS. ZnO/GaN heterojunction LEDs based on ZnO nanowires/p-GaN and ZnS@ZnO core–shell nanowires/p-GaN were designed and fabricated. A highly efficient LED with an UV EL emission peak of 378 nm has been obtained. Analysis of EL spectra and band diagram indicated that the captured electrons and holes caused by localized states can form localized excitons, which should account for the realization of UV EL emission. Our investigation could lead to another high performance emitting device.

### ASSOCIATED CONTENT

* Supporting Information
  
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b08961.

  Current–voltage characteristic of two heterojunctions; additional EL spectra (PDF)

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#### Notes

The authors declare no competing financial interest.

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**Figure 5.** (a) EL spectra of ZnO nanowires/p-GaN heterojunction under 10.0 V; (b) EL spectra of ZnS@ZnO core–shell nanowires/p-GaN heterojunction under 10.0 V; (c) schematic diagrams of carrier recombination and energy band schematic diagram of ZnO nanowires/p-GaN heterojunction; (d) schematic diagrams of carrier recombination and energy band schematic diagram of ZnS@ZnO core–shell nanowires/p-GaN heterojunction.
References


