Interfacial Emission Adjustment in ZnO Quantum Dots/p-GaN Heterojunction Light-Emitting Diodes

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Supporting Information

ABSTRACT: Ultraviolet (UV) light-emitting diodes (LEDs) were made by using ZnO quantum dots (QDs) as the emission layer. ZnO QDs with the diameter of 5 nm were fabricated by using a simple sintering method. By using p-GaN as the hole injection layer, a ZnO QDs/p-GaN heterojunction LED was constructed. Trap-controlled SCLC behavior of QDs led the LED to emit light mainly from the QDs layer, and the direct physical contact between ZnO QDs and GaN could effectively reduce the interfacial emission. As the result, a UV LED with the electroluminescence wavelength of 382 nm has been achieved.

■ INTRODUCTION

ZnO-based light-emitting diodes (LEDs) have been considered as one of the most promising candidates for the next generation of blue/near-UV light sources, which are expected to realize a wide range of applications including solid-state lighting, food sterilization, water and air purification, etc.¹ While the pursuit of stable and reproducible p-ZnO is still undergoing,^{2,3} heterojunctions of n-ZnO/p-GaN are employed as an alternative approach in this regard by considering the similar crystallographic and electronic properties of ZnO and GaN. Many research efforts have been already focused on the preparation of n-ZnO/p-GaN heterojunction LEDs. Also, many kinds of ZnO structures have been investigated, such as ZnO thin films,⁴ nanorods,^{5–7} nanowires,^{8–11} etc. Yet the red-shift of ZnO near band edge (NBE) emission, radiative interfacial recombination, and defective emission are often found in the devices. Furthermore, the electroluminescence (EL) of the ZnO/p-GaN heterojunction LEDs emits mainly from the interface between ZnO and GaN, or from the p-GaN side instead of the ZnO, because the electron injection from ZnO would prevail over the hole injection from p-GaN due to the higher carrier concentration in n-ZnO.¹² As the result, the emission wavelengths of these devices are always longer than 390 nm,⁴⁻¹⁰ which is out of the UV region. The lack of UV emission in ZnO heterojunction LEDs has limited its broader range of applications. To solve these problems, some researchers have employed wide band gap materials, like MgO,¹³ AlN,^{14,15} or HfO₂,¹² as the intermediate layer between the ZnO and GaN to reduce the radiative interfacial recombination and block the electron injection from ZnO. Yet the EL wavelengths have still not blue-shifted into the UV



region. At the same time, the intermediate layer has blocked the hole injection from p-GaN.

Therefore, we thought to use ZnO quantum dots (QDs) as an emitter to obtain pure UV EL. Because of their properties of narrow emission line widths, high quantum yield, and superior photostability, semiconductor ODs have been considered as an ideal material for the function layer of LEDs.¹⁶⁻¹⁸ Most importantly, the size-tunable luminescence character of ODs will lead the emission peak to further blue shift to shorter wavelengths, which makes it possible to realize a LED with pure UV emission. Meanwhile, due to the huge surface-to-volumeratio of QDs, the electronic conduction in QDs is expected to follow the trap-controlled space charge limited current (SCLC) behavior.^{19,20} The surface traps of QDs will restrict carriers' flowing, which will lead the LEDs to emit light mainly from the QDs layer. In recent years, several groups have reported the synthesis of ZnO QDs through liquid-phase reaction,²¹⁻²³ but due to the surface and inner defects of ZnO QDs that were introduced during the wet chemical synthesis procedure, the emission peaks of QDs are usually dominated by the visible light, and no UV emission has been observed. As the result, there are few reports on ZnO QDs-based UV LEDs.

Here in this work, we demonstrate a new sintering method to prepare the ZnO QDs with UV emission. The QDs were synthesized on the electrode directly, and thus decreased the interface defects between electrode and QDs, and consequently a contact with better electrical properties was obtained. When the ZnO QDs film and p-GaN were fixed together, a ZnO

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QDs-based LED was made. By using the method introduced here, the radiative interfacial recombination at ZnO/GaN interface has been effectively reduced and the EL of the device is mainly from ZnO NBE emission. A ZnO QDs-based LED with an emission peak of 382 nm and a fwhm (full width at half-maximum) of 17 nm has been achieved.

EXPERIMENTAL SECTION

Synthesis of ZnO QDs on Substrate. The sintering method introduced here is similar to the synthesis process of NiO particles reported by Zhou et al.²⁴ In this work, ITO glass substrates were ultrasonically cleaned with acetone, ethanol, and deionized water for 15 min, respectively. Subsequently, the substrates were treated by oxygen plasma cleaner for 5 min. Zinc acetate without crystal water $(Zn(CH_3COO)_2, Aldrich, 99.99\%)$ was dissolved in ethanol to form a solution with the concentration of 30 mg per milliliter. The zinc acetate solution was spin-coated on ITO glass substrates. The substrates then were sintered at 400 °C in a tube furnace for 15 min. Zinc acetate decomposed to form ZnO QDs on the substrate surface. The process of spin-coating and sintering was repeated four times. We also prepared ZnO QDs film on p-GaN using the same method.

Preparation of EL Device. The LEDs were assembled from the thin films of ZnO QDs grown on ITO substrates. Previously reported ZnO/p-GaN heterojunction LEDs were constructed by growing ZnO nanostructures on p-type GaN substrates first, and then an electrode was made on top of the ZnO structure.²⁵ Yet in this work, ZnO QDs were directly synthesized on the electrode, then contacted with p-GaN film. The p-GaN thin film on the c plane sapphire used in this experiment was grown by MOCVD method with magnesium as the dopant. The carrier density of the p-GaN film is 2.44×10^{17} cm⁻³. To provide ohmic behavior of the contacts, Ni/Au electrodes with thicknesses of 10 and 90 nm were prepared on the p-GaN surface by metal thermal evaporation method under the pressure of 2×10^{-3} Pa. Before evaporation, p-GaN was ultrasonically cleaned with acetone, ethanol, and deionized water for 10 min, respectively. To construct the LED, the ITO glass that has been coated with ZnO QDs was placed face to face on the p-GaN thin film. Subsequently, they were fixed together by binder clips to form a close and fine physical contact. The fabrication method was also applied to ZnO QDs coated GaN device. First, ZnO QDs were sintered on the p-GaN substrate, then the ITO electrode was put on the top of the QDs film, and they were also bound together with binder clips. The reference devices of ZnO nanorods were made by growing ZnO nanorods on p-type GaN substrates and then binding the ITO glass on top of the ZnO.

Characterizations. The morphology of ZnO QDs was investigated by field emission scanning electron microscopy (FESEM: Hitachi S-4800). The high-resolution transmission electron microscope (HRTEM) in this work was obtained on JEOL JEM-2100F equipment. The room-temperature photoluminescence (PL) spectra measurements were carried out by using a He–Cd laser and the micro-Raman spectrometer; the excitation line wavelength of He–Cd laser was 325 nm. The absorption spectra were carried out using a Shimadzu UV-3101 PC spectrophotometer. The EL spectra of our devices were performed by using a fluorescence spectrophotometer (Hitachi F4500). The current–voltage (I-V) characteristic curves of the devices were measured by a Keithley 2611A measurement system.

RESULTS AND DISCUSSION

Figure 1a shows the FESEM image of ZnO QDs grown by the sintering method. From the picture, we can see that the



Figure 1. (a) FESEM image of ZnO QDs prepared by sintering method. (b) HRTEM image of the QDs.

morphology of QDs has the character of single size and homogeneous distribution. In addition, there is no agglomeration between particles. Figure 1b exhibits the HRTEM image of the QDs; as can be seen from the figure, the clear lattice with 0.26 nm spacing in the image corresponds to the (0002) planes of wurtzite ZnO. Also, the average diameter of ZnO QDs is about 5 nm.

Figure 2 shows the room-temperature absorbance and PL spectra of the ZnO QDs layer. On the absorbance curve, we can clearly see the first exciton absorption peak located at 360 nm, which is similar to the absorbance spectra of other high-quality QDs.²⁶ The band gap of QDs calculated from the absorption spectrum is 3.50 eV. The PL peak of ZnO QDs locates at 370 nm, which has blue-shifted markedly as compared to ZnO thin films and nanowires.^{27–29} The blue shift of the band gap and the emission peak can be explained by the quantum size effect.^{30–32} When the size of the ZnO particles reduces to the Bohr radius of excitons, the quantum confinement effect is enhanced.³³ The function of states density for conduction and valence bands changes, and the band gap energy increases. It causes the blue shift of emission peak. We introduce the model excited electronic states of sufficiently



Figure 2. Room-temperature PL and absorbance spectra of ZnO QDs.

smaller semiconductor crystallites derived by Brus.³¹ The band gap energy of QDs can be estimated by the following equation:

$$E(\text{dots}) = E(\text{bulk}) + \frac{h^2}{8R^2} \left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0} \right) - \frac{1.8e^2}{4\pi\varepsilon\epsilon_0 R}$$

where E(bulk) is the band gap energy of ZnO bulk structures that have weak quantum effects, *h* is Planck's constant, *R* is the radius of QDs, $m_e*(m_e*=0.24)$ and $m_h*(m_h*=0.45)^{34}$ are the effective mass of electrons and holes, m_0 is the mass of free electron, *e* is the charge on an electron, ε_0 is the permittivity of free space, and ε is the relative permittivity. The value of ZnO E(bulk) is considered to be 3.37 eV.^{27–29} From the equation, we work out that the value of E(dots) is equal to 3.48 eV, which is consistent with our experimental results calculated above. In addition, the QDs have hardly any emission in the visible area. We can conclude that the ZnO QDs have high crystallinity and few defects. They are ideal materials to prepare UV LEDs.

Because the ZnO ODs have pure UV emission and the emission wavelength has blue-shifted as compared to bulk materials, it can be used as the function laver of UV LEDs. First, ZnO QDs were sintered on the ITO glass, which served as the top electrode. Subsequently, a p-GaN substrate was placed on the ZnO QDs surface to form a physical contact with the QDs layer, and then the device was fixed. The schematic diagram of this device is shown in Supporting Information Figure S1(a). The I-V characteristic curve of this device is shown in the inset of Figure 3a. It displays a prefect rectification performance, and the threshold voltage is 3.5 V. Supporting Information Figure S2 shows the ohmic contact between Ni/ Au electrode and p-GaN, which demonstrates that the shape of the I-V curve in Figure 3a is dominated by the junction formed in the device. This indicates that ZnO and GaN have formed a good p-n junction. When the forward bias is higher than 4 V, the UV emission is obtained. The EL spectra are shown in Figure 3a. Only one peak centered at 382 nm is observed. As compared to the light-emitting peak position of previous reports,⁴⁻¹⁵ the present emission peak has blue-shifted greatly. The luminescence intensity increases with voltage, but the position of the EL peak does not change. So we could conclude that this device has a good performance of carriers injection and emission stability.

Article



Figure 3. (a) EL spectra of the device prepared by ZnO QDs coated ITO glass and p-GaN thin film; inset is the I-V curve of the device. (b) Gaussian fitting result of this device under 22 V bias; inset is an image of the light emission at room temperature.

To further study the performance of this device, Gaussian fitting was used to analyze the emission spectrum. Figure 3b shows the Gaussian fitting results of our device under 22 V bias. The emission peak consisted of four parts. As previously reported, the peak centered at 407 nm comes from the radiative interfacial recombination of the electrons from n-ZnO and holes from p-GaN.^{9,10} The peak located at 382 nm is attributed to the NBE emission in $\bar{Zn}O$ QDs that originates from the recombination of ZnO free and bound excitons. Because of the quantum confinement effect of ZnO QDs, the emission peak that originates from the NBE emission of ZnO has blue-shifted to 382 nm as compared to thin film and nanowire devices.^{4–10} Furthermore, because of the trap-controlled SCLC behavior, the predominance of ZnO emission is more evident (as compared to refs 8-10 and the nanorods device mentioned in the Supporting Information). In addition, peaks centered at 418 and 361 nm have also been observed. As shown in Supporting Information Figure S3, the PL spectrum of p-GaN thin film consists of two parts: NBE emission centered at 360 nm and a broad defective emission ranging from 410 to 460 nm. So the peak located at 418 nm in Figure 3b is considered to originate from the transition of electrons on p-GaN conduction band to Mg²⁺ doping level. Taking into consideration that the physical

contact has formed between ZnO QDs and p-GaN, the forward injection of carriers is highly efficient as we see from the I-V curve in Figure 3a, which means the blocking of carriers at the interface has been eased. Meanwhile, because the barrier heights at the interface for the holes (0.57 eV) and for the electrons (0.59 eV) are almost equal,⁸⁻¹⁰ the ease of carriers blocking has caused more electrons in ZnO to diffuse across the interface and migrate into the p-GaN layer, so we could obtain a tiny peak originating from the NBE emission of GaN. Therefore, this device is a high performance UV LED.

The ability to manipulate the electronic properties of semiconductor surfaces and interfaces, which is one of the most fascinating problems of condensed-matter science, is of significant technological importance. The interface of semiconductor materials could greatly influence the properties of devices, and there has been much research on interfacial emission.^{35–37} To certify the impact of interface layer on the device performances, ZnO QDs were directly prepared on p-GaN and form a simple physical contact with ITO substrate. The schematic diagram of this device is shown in Supporting Information Figure S1(b). The inset of Figure 4a shows the I-V characteristic curve of this device, and we can find that the rectification characteristic is not perfect. The threshold voltage is about 5.5 V, while the emission open voltage is 10 V. Figure 4a shows the room-temperature EL spectra of this device under 10-25 V bias. The emission locates at 387 nm. Figure 4b shows the Gaussian fitting results of the second device under 25 V bias. The emission peak also can be divided into three parts: the peak at 385 nm is originating from the recombination of electrons in ZnO with hole transition from p-GaN, the peak centered at 401 nm can be attributed to the recombination of carriers in the interface of ZnO and p-GaN, and the peak located at 436 nm originated from the transition of electrons on p-GaN conduction band to Mg²⁺ doping level. From the fitting results, we could see that due to using QDs as a function material, the emission wavelength of ZnO has also blue-shifted to 385 nm as compared to thin film and nanowire devices, but the interfacial emission is strong. As the result, the final emission wavelength has red-shifted from 382 to 387 nm. It is worth noting that the operating voltage of the device is much higher than that of the other two devices mentioned above, and the interfacial emission peak has blue-shifted from 407 to 401 nm. This is due to the sintering process on p-GaN film. When we sintered the ZnO QDs onto the p-GaN film, the interface between ZnO and GaN has suffered the annealing process of 400 °C; the annealing has accelerated the formation of Ga–O bonds, Zn–N bonds, 38,39 and ZnGa₂O₄^{12,40} alloy layer at the interface. The ZnGaO₄ alloy has a wider band gap of 4.4-5.0 eV,¹² it blocks the injection of carriers and changes the interfacial luminescence center, and, as a result, the operating voltage is higher and the interfacial emission peak has blueshifted.

Considering the above analyses, we could conclude that among the simulated multiple peaks of the devices, the most critical influence of the final peak position is the interfacial emission. From the experimental results mentioned above, we could see that when the intensity of interfacial emission is strong, the intensity ratio of ZnO NBE emission to interfacial emission is small, and the overall emission wavelength of the device is longer than 390 nm. We could infer that when we grew ZnO nanostructures on GaN substrate by chemical method or sintering method, Zn^{2+} ions could diffuse into GaN layer, Ga–O bonds, and Zn–N bonds, and interstitial and



Figure 4. (a) EL spectra of the device prepared by ZnO QDs coated GaN and ITO glass; inset is the I-V curve of the device. (b) Gaussian fitting results of the device under 25 V bias.

vacancy defects could be formed during the synthesis process, which consequently result in the blocking of carriers and strong interfacial emission. Yet the direct physical contact could greatly prevent the formation. After we replaced the chemical contact between ZnO and p-GaN layer by physical contact, the bonds, alloy, interstitial defects, and vacancy defects have been eliminated, and only dislocation and stacking faults remained at the interface. So the intensity ratio between ZnO NBE emission and interfacial emission has increased in Figure 4b, which means the radiative interfacial recombination has been suppressed. Meanwhile, due to the trap-controlled SCLC behavior, the EL emission occurs predominantly in the ZnO QDs layer. Therefore, the EL wavelength of the device has blue-shifted to shorter than 390 nm. The experimental results in this Article have proved that the interfacial defects could greatly affect the emission peak of LEDs and the physical contact introduced in this work could improve the performance of ZnO heterostructure devices.

CONCLUSION

In summary, by using a simple sintering method, ZnO QDs with UV emission have been fabricated. Because of the quantum effects, the PL wavelength of ZnO QDs has blueshifted by 10 nm as compared to ZnO nanowires. After we sintered the QDs layer directly on the ITO electrode and fixed it together with p-GaN substrate, a high performance UV LED with an EL emission peak of 382 nm has been obtained. Because of the trap-controlled SCLC behavior of QDs, the EL of LEDs emitted mainly from the QDs layer. The direct physical contact between ZnO QDs and GaN layer has prevented the formation of alloy, Ga-O bonds, Zn-N bonds, interstitial, and vacancy defects at the interface. As the result, the interfacial emission has been effectively eliminated, and the electroluminescence wavelength has blue-shifted to 382 nm. The methods and discussions mentioned here will give a new way to solve the interface problem of semiconductors and enhance the performance of photoelectric devices.

ASSOCIATED CONTENT

S Supporting Information

Schematic diagram of the device, the I-V curve between p-GaN thin film and Ni/Au electrode, the room-temperature PL spectrum of p-GaN thin film, the FESEM image of ZnO nanorods, the EL spectra of the device prepared by ZnO nanorods and p-GaN under different applied voltages, and the Gaussian fitting results of the device under 14 V bias. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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