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Light-emitting diodes fabricated from small-size ZnO quantum dots

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ABSTRACT

Zinc oxide (ZnO) quantum dots (QDs) have been fabricated. High-resolution transmission electron microscopy shows that the ZnO QDs have a narrow size distribution, and are highly crystallized with wurtzite structure. Light-emitting diodes have been constructed by employing the QDs as active layers. Intense near-band-edge emissions have been observed from the diodes, which show a noticeable blue-shift compared with the emission of a similar diode employing ZnO film as an active layer, which is demonstrated to come from the quantum size effect of the QDs due to their small size.

1. Introduction

Quantum dots (QDs) have shown promise as the active layers in light-emitting diodes (LEDs) because of their size-tunable band-gaps, high quantum efficiencies, and compatibility with solution processing methods [1,2]. The most noteworthy property of semiconductor QDs lies in its size-dependent electrical and optical properties, known as quantum size effect [3]. Zinc oxide (ZnO) has been studied extensively in recent years for its wide bandgap (3.37 eV) and large exciton binding energy (60 meV), which is greatly advantageous for applications in ultraviolet (UV) light-emitting diodes and low-threshold lasers [4–9]. Additionally, ZnO has been one of the most active materials in nanoscience and nanotechnology because it can be fabricated into various nanostructures in relatively simple ways [10–12]. Among the rich family of ZnO nanostructures, zero-dimensional ZnO QDs are expected to offer unique optical properties owing to their three-dimensional confinement to carriers and photons, which may lead to a notable enhancement in the performance of light-emitters. Although some reports on electroluminescence (EL) from ZnO based nanostructures have been demonstrated [5,6,13], none of them has demonstrated quantum size effect in EL emission. That is, the most noteworthy property of QDs has not been fulfilled for ZnO based nanostructures.

In this paper, ZnO QDs have been prepared by sol–gel method, and ZnO-QDs/MgZnO/*p*-GaN structured LEDs employing the QDs as active layers have been constructed. The emission of the structures shows obvious quantum size effect compare with a similar LED structure employing ZnO film as the active layer.

2. Experimental sections

The ZnO QDs were prepared in a sol–gel method developed by Spanhel and Anderson [14]. A commercial available *p*-GaN/sapphire template was used as a substrate for the growths. A thin MgZnO layer was deposited onto the substrate in a metal–organic chemical vapor deposition technique. Subsequently, the ZnO QDs were dip-coated onto the MgZnO/*p*-GaN/sapphire template (referred as QDs-LED). For comparison, another ZnO-film/MgZnO/*p*-GaN/sapphire LED was also fabricated using a VG V80H molecular-beam epitaxy system (referred as Film-LED).

The morphology and structure of the samples were characterized by transmission electron microscopy (TEM, Philip CM200-FEG) and field-emission scanning electron microscopy (SEM, Hitachi S-4800). The absorption spectra were recorded in a Shimadzu UV-3101PC spectrometer. The photoluminescence (PL) spectra were measured in a JY-630 spectrometer employing the 325 nm line of a He–Cd laser as the excitation source, and EL measurements were performed in a Hitachi F4500 spectrophotometer. The current–voltage (*I*–*V*) characteristics of the devices are characterized in a Lakeshore 7707 Hall measurement.

3. Results and discussion

Fig. 1(a) illustrates the TEM image of the ZnO QDs. The image shows clearly that the QDs have nearly spherical shape. A histogram of the size-distribution of the QDs obtained by analyzing 300 dots from the

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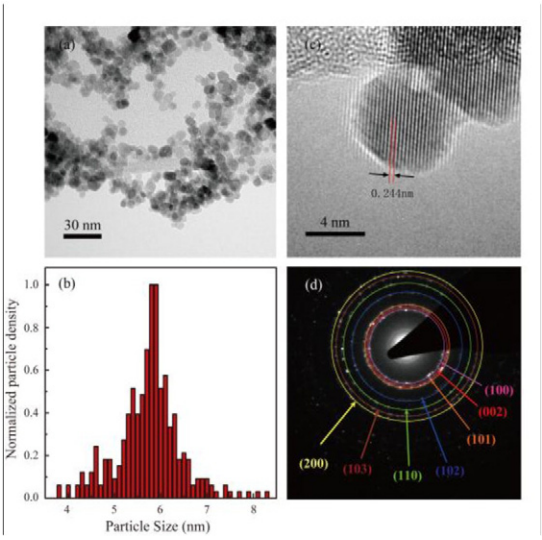

Fig. 1. Low-magnification TEM image (a), high-magnification TEM image (b) histogram of the size distribution (c), and SAED pattern (d) of the ZnO QDs.

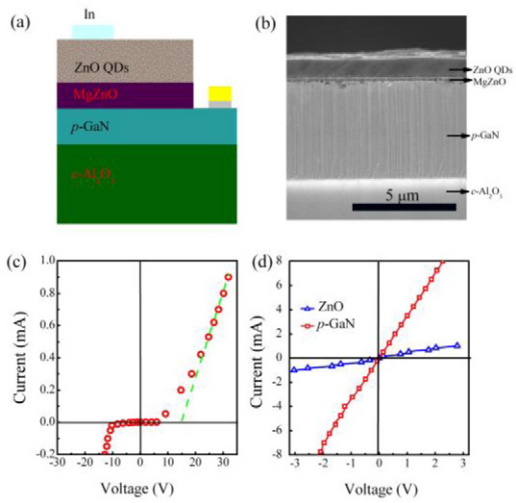

Fig. 3. Schematic diagram (a) and cross-sectional SEM image (b) of the ZnO QDs LED; (c) *I–V* characteristics of In and Au/Ni contacts on ZnO QD and *p*-GaN, respectively; (d) *I–V* curve of the ZnO QDs LED.

TEM image is shown in Fig. 1(b), from which a mean diameter of 5.8 ± 0.6 nm (σ = 10%) is determined. Fig. 1(c) and (d) shows the high-resolution TEM image and corresponding selected area electron diffraction pattern of the QDs. The pattern exhibits well-distinguished concentric rings, and the lattice spacing between adjacent planes is about 0.244 nm, which corresponds to the *d*-spacing of the (101) crystal plane of wurtzite ZnO. The TEM image indicates that the ZnO QDs are highly crystallized wurtzite nanocrystallites with a narrow size-distribution. Note that the narrow size-distribution lays a solid ground for the future optical study of quantum size effect.

The absorption and PL spectra of the 5.8 nm ZnO QDs are shown in Fig. 2(a) and (b), and those of a ZnO film are also displayed for comparison. From the absorption spectra, one can find that the 5.8 nm ZnO QDs exhibit an excitonic absorption feature at around 341 nm, which is blueshifted by about 21 nm compared with the absorption peak of the ZnO film. For the PL spectra, the emission of the QDs is located at about 362 nm, while that of the film is at 377 nm. That is, both the absorption and PL spectra of the 5.8 nm ZnO QDs show a noticeable blueshift compared with those of the film.

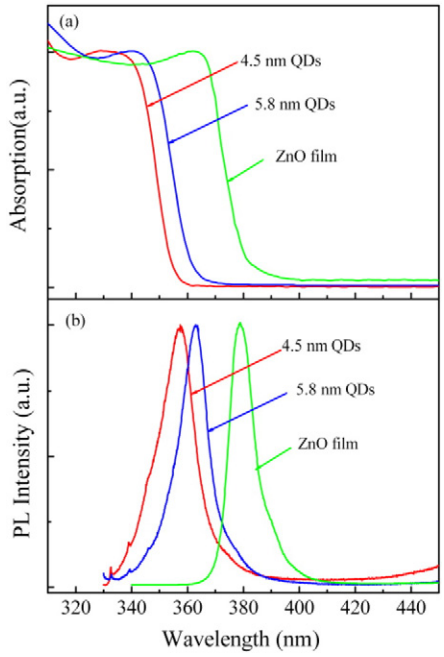

Fig. 2. (a) Absorption and (b) PL spectra of the 4.5 nm QDs, 5.8 nm QDs, and ZnO film.

It is accepted that the bandgap of a QD can be expressed by the following formula [15]:

$$E^* \cong E_g^{\text{bulk}} + \frac{\hbar^2\pi^2}{2er^2}\left(\frac{1}{m_e^* m_0} + \frac{1}{m_h^* m_0}\right) - \frac{1.8e}{4\pi\varepsilon\varepsilon_0 r} \quad (1)$$

where E^* and E_g^{bulk} are the bandgap of ZnO QDs and bulk material, respectively, $\hbar$ is Plank constant divided by 2π, r is the radius of the QD, m_e^* and m_h^* are the effective mass of electrons and holes, m_0 and e is the mass and elementary charge of an electron, ε and ε_0 is the relative permittivity and permittivity in free space. Considering that the bandgap of ZnO is 3.37 eV, the effective mass of electrons and holes of ZnO is 0.24 m_0 and 0.45 m_0, respectively, the mean diameter of the ZnO QDs is 5.8 nm, and the relative permittivity of ZnO is 3.7 [16], a bandgap of 3.433 eV can be derived from Eq. (1) for the QDs. The derived value is in reasonable agreement with the value determined from the absorption spectrum (3.459 eV), confirming that the blueshift observed in PL and absorption spectra comes from the quantum size effect caused by the small size of the QDs.

While quantum size effect has been observed in the PL and absorption spectra of the 5.8 nm ZnO QDs, it will be more interesting

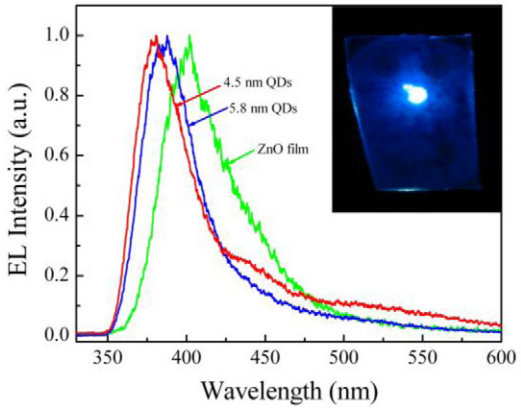

Fig. 4. Room temperature EL spectra of the LEDs employing the 4.5 nm QDs, 5.8 nm QDs and ZnO film as active layers under the injection current of 0.9 mA. The inset shows the emission photograph of the 5.8 nm ZnO QDs LED.

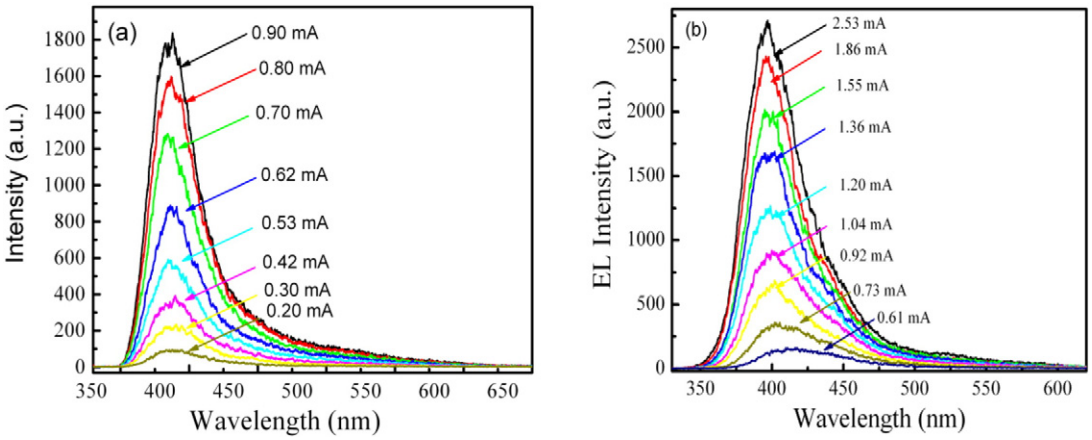

Fig. 5. EL spectra of the 5.8 nm QDs-LED and those of the Film-LED at various injection current.

if the effect can be observed in EL. However, none such report can be found. To this end, a LED structure employing the 5.8 nm QDs as the active layer has been constructed. Fig. 3(a) and (b) shows the schematic diagram and cross-sectional SEM image of the QDs-LED. The thicknesses of the ZnO QDs, MgZnO and GaN layers are 700 nm, 100 nm and 5 μm respectively. Note that the Mg composition in the MgZnO layer is 0.5. The effect of the $Mg_{0.5}Zn_{0.5}O$ layer is to confine electrons into the ZnO layer, while holes can tunnel through the layer under the drive of forward bias, and the detailed elucidation of this process can be found in our previous papers [9,17]. The *I–V* curve of the QDs-LED was shown in Fig. 3(c). Obvious rectifying behavior with a turn-on voltage of about 14.0 V is observed. The linear curves for both Ni/Au on *p*-GaN and In on ZnO reveal that ohmic contacts have been obtained in both electrodes, as shown in Fig. 3(d).

The EL spectra of the 5.8 nm ZnO QDs-LED and Film-LED at the same injection current of 0.9 mA is illustrated in Fig. 4, and the emission photograph of the 5.8 nm ZnO QDs-LED is shown in the inset of Fig. 4, obvious blue emission can be observed by bare eyes from the LED. The spectrum of the 5.8 nm QDs-LED exhibits a strong emission at 385 nm, which displays a notable blueshift compared with the emission of the Film-LED (403 nm). To explore the origin of the blueshift, ZnO QDs with a mean diameter of 4.5 nm have also been prepared, and the absorption and PL spectra of the 4.5 nm ZnO QDs blueshift compared that of the 5.8 nm QDs and film, as shown in Fig. 2(a) and (b). The ZnO QDs/MgZnO/*p*-GaN LED structure employing the 4.5 nm QDs as an active layer has also been constructed, and the LED shows an emission at around 379 nm, as shown in Fig. 4. Note that the EL of the 4.5 nm QDs present blueshifts further compared with that of the 5.8 nm QDs. From the above facts, one can conclude that the blueshift observed in the EL spectra of the LEDs comes from quantum size effect due to the small size of the QDs.

The EL spectra of the 5.8 nm QDs-LED and Film-LED at difference injection current are shown in Fig. 5. As evidenced from the figure, the EL spectra of the QDs-LED shift little, but those of the Film-LED blueshift gradually with increasing the injection current. The dependence of the EL peak position on injection current is determined mainly by two factors, the temperature-rise caused by the heating effect and the filling of higher energy levels by carriers, and the former will cause redshift, while the latter will cause blueshift. The dependence of the EL position on the injection current is the combination effect of these two factors.

4. Conclusion

In summary, small-sized ZnO QDs have been prepared, and the QDs are highly crystallized in wurtzite structure. LED structures have been constructed from the QDs, and the emission of the ZnO QDs shows obvious blueshift compared with that of the ZnO film, and the blueshift can be attributed to the quantum size effect caused by the small size of the QDs. This is the first report on ZnO based LEDs showing quantum size effect that is the most noteworthy property of a nanostructure, thus may provide a clue for the realization of high-performance ZnO based light-emitters.

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