White Light Generation With CdSe–ZnS Nanocrystals Coated on an InGaN–GaN Quantum-Well Blue/Green Two-Wavelength Light-Emitting Diode

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***Abstract*—We grew and processed a blue/green two-wavelength light-emitting diode (LED) based on the mixture of two kinds of quantum wells (QW) in epitaxial growth. The X-ray diffraction and photoluminescence measurements indicated that the crystalline structure and the basic optical property of individual kinds of QW are not significantly changed in the mixed growth. The relative electroluminescence (EL) intensity of the two colors depends on the injection current level, which controls the hole concentration distribution among the QWs. At low injection levels, the top green-emitting QW dominates in EL. As the injection current increases, the blue-emitting QWs beneath become dominating. We also coated CdSe–ZnS nanocrystals on the top of the two-wavelength LED for converting blue photons into red light. With the coating of such nanocrystals, the device emits blue, green, and red lights for white light generation.**

***Index Terms*—Light-emitting diode (LED), nanocrystal, white light generation.**

BECAUSE of the important applications of solid-state lighting and liquid-crystal display (LCD) backlighting, recently the development of semiconductor white light devices has attracted much attention. Currently, such development mainly focuses on the use of phosphors for converting either blue or UV photons from a single-color light-emitting diode (LED) into long-wavelength light for white light mixing. However, the use of phosphors for white light generation leads to the disadvantages of lower efficiency, process complication, patent control, and environmental issue. Therefore, the fabrication of phosphor-free, single-chip, all-semiconductor white light LEDs has become an important trend [1]–[4]. For this purpose, multiple-wavelength LEDs by stacking InGaN–GaN quantum wells (QWs) of different compositions and/or geometries are of great interest [1],[2]. Nevertheless, stacking such QWs of different types is not straightforward because they are usually highly strained. The growth order of different QWs and the in-between barrier thickness can affect the emission wavelength of each QW [3]. In particular, the strain distribution controls the quantum-confined Stark effect (QCSE), which leads to emission spectral blue shift as the injection current increases. Hence, a careful design of such a QW structure is needed.

For mixing colors to obtain white light of a high rendering index, currently the major difficulty is the low emission efficiency of red-emitting InGaN compounds [2]. Although the high-efficiency red emission from an InGaN–GaN nanocolumn structure has been reported, the process procedures for fabricating such a white light LED can be quite complicated [5]. Before efficient red-emitting InGaN compounds for easy integration with blue- and green-emitting structures can be available, a photon down-conversion material is still needed. In particular, a material for converting blue photons into red light is very useful. Although phosphors for converting UV photons into red light exist, that for efficiently converting blue photons into red light has not been reported yet. Recently, it has been proved that the use of CdZe–ZnS nanocrystals for such conversion is quite attractive [6], [7]. Basically, such a crystal of a few nanometers in diameter functions as a quantum dot. It can efficiently absorb light in the range from UV through blue and re-emit red light. Its absorption and emission spectra can be easily tuned through controlling its size.

In this letter, we first demonstrate the growth and fabrication of a blue/green two-wavelength LED by stacking four QWs of two different growth conditions. Then, we show white-light generation by coating CdSe–ZnS nanocrystals on such a two-wavelength LED for converting blue photons into red light.

The epistructure of the blue/green two-wavelength LED was grown with a metal–organic chemical–vapor deposition reactor with the following procedures. After the growth of a 25-nm nucleation layer (grown at 535 °C), a 2-μm n-GaN (5×10^{18} cm^{-3} in silicon-doping concentration) was deposited at 1070°C. Then, two QW growth conditions are considered: 1) temperature at 690 °C, wafer carrier rotation at 750 r/min, and gas flow rates at 3000 sccm for N_2 and 3000 sccm for NH_3 and 2) temperature at 710 °C, wafer carrier rotation at 1500 r/min, and gas flow rates at 1000 sccm for N_2 and 1500 sccm for NH_3. The first and second growth conditions were designed for the growths of the green- and blue-emission QWs, respectively. All the well thickness is about 3 nm. With the different growth conditions above, the indium compositions are different, leading to the emissions of different colors. Purely blue or green LEDs have been fabricated based on the growth of five QWs of the same conditions. In the mixed QW

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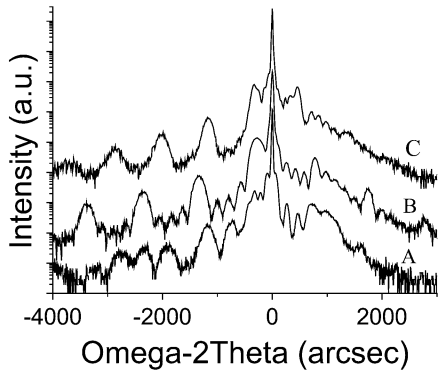

Fig. 1. XRD patterns of epitaxial structures of (A) two-wavelength LED, (B) purely blue LED, and (C) purely green LED.

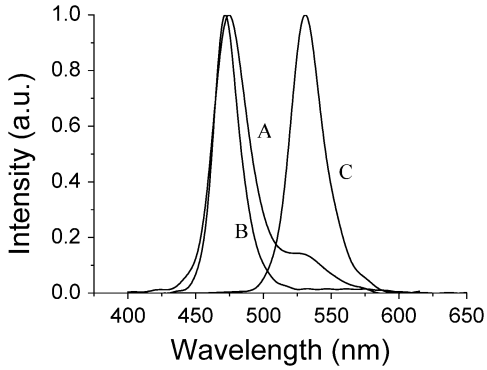

Fig. 2. Room-temperature PL spectra of (A) two-wavelength LED, (B) purely blue LED, and (C) purely green LED.

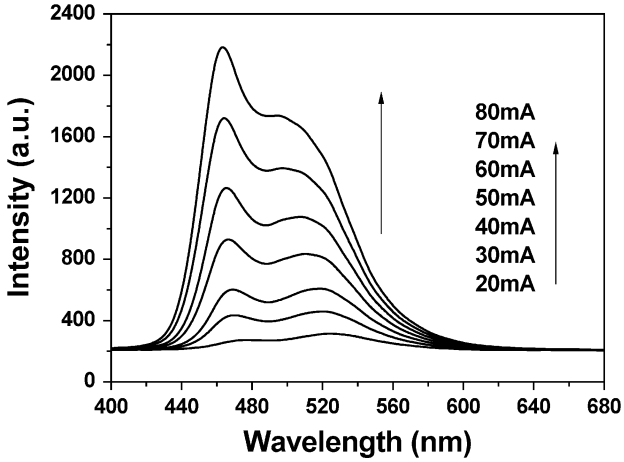

Fig. 3. Room-temperature EL spectra of two-wavelength LED at various injection current levels.

sample, we arranged the QW sequence as (from the bottom) green/blue/blue/green in the four-QW structure. The lower GaN barrier below the bottom (green) QW has the thickness of 16 nm and was grown at 800 °C with the silicon-doping concentration of 7×10^{17} cm^{-3}. Among the rest four barrier layers, the first two (from the top) have the thickness of 6 nm and the next two have the thickness of 16 nm. In the deposition of a 6-nm barrier layer, after the growth of a ∼2-nm GaN cap layer at the same temperature as that for the last well layer, the growth was interrupted. During the interruption, the wafer temperature was ramped to 800 °C and H_2 of 500 sccm was added to the growth chamber [8]. After the interruption, a 4-nm GaN layer was grown to form a 6-nm barrier. The procedures for depositing a 16-nm barrier were the same as those for a 6-nm barrier except that a 14-nm GaN layer was grown at 800 °C after the growth interruption. The growth of the GaN cap layer between the InGaN well and the higher temperature GaN barrier meant to protect the InGaN well from indium desorption during the temperature ramping and the H_2 addition. The smaller barrier thicknesses close to the p-type layer were designed to enhance hole trapping into the deeper QWs. After the growth of the four QWs, a 20-nm p-$Al_{0.2}Ga_{0.8}N$ layer, followed by a 120-nm p-GaN layer (both grown at 930 °C), was deposited. LEDs based on the mixed QW epistructure were then fabricated with the standard procedure. Ni (15 nm)/Au (150 nm) were used for the p-type Ohmic contacts. Also, Ti (15 nm)/Al (75 nm)/Ti (15 nm)/Au (150 nm) were used for the n-type Ohmic contacts. Meanwhile, thin metal layers of Ni (5 nm)/Au (5 nm) cover the whole top surface for enhancing current spreading in a device.

Fig. 1 shows the X-ray diffraction (XRD) pattern of the LED epistructure of mixed QWs (curve A). For comparison, curves B and C for a purely blue-emitting QW (five periods) sample and a purely green-emitting QW (five periods) sample, respectively, are also shown. The major sharp peak near the center represents the GaN contribution. One can see that in curves B and C, periodical secondary peaks clearly demonstrate the QW periodicity. Also, the visible third-order peaks in the purely blue sample indicate the reasonably good QW quality in this sample. In the sample of mixing the two kinds of QW, the major XRD peaks roughly correspond to those of the two single-color samples, indicating that basically the superposition principle can be applied to these XRD measurements. This correspondence implies that the two kinds of QW structure were not significantly influencing each other when they were stacked on a wafer. However, the details of the XRD pattern in the mixed QW sample deserve further investigation because XRD measurement cannot follow closely the superposition principle, as clearly shown in Fig. 1 [9].

Fig. 2 shows the room-temperature photoluminescence (PL) spectra of the mixed QW epistructure (curve A), the purely blue-emitting (curve B), and the purely green-emitting (curve C) QW samples. In the mixed-QW sample, one can see the strong PL peak of blue light at around 470 nm and a relatively weaker green peak at around 530 nm. The two-color peaks correspond well to the PL peaks of the single-color samples. In the two-color sample, the PL contribution of the top green-emitting QW is small although the photo-generated carrier density in this QW is expected to be the highest in our top-excitation PL measurement. This result indicates the poorer crystalline quality of the green-emitting QW.

Fig. 3 shows the room-temperature electroluminescence (EL) spectra of the fabricated two-wavelength LED at various injection currents. One can clearly see the two major peaks, corresponding to the blue and green emissions at 460 and 520 nm, respectively. The corresponding PL wavelengths are longer than the EL ones by about 10 nm [10]. The blue EL peak shifts by less than 10 nm when the injection current increases from 20 to 80 mA. The corresponding shift of the green EL peak is

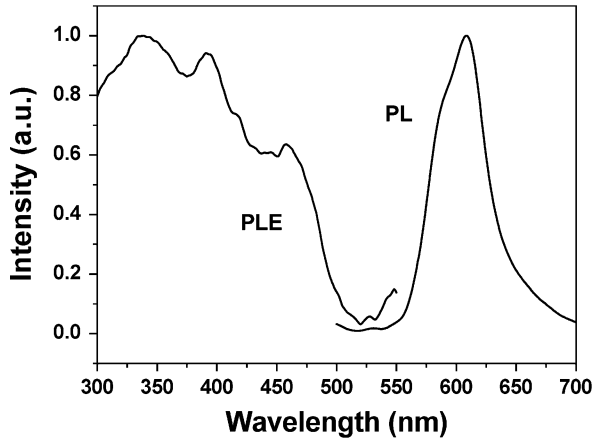

Fig. 4. Room-temperature PL and PLE spectra of CdSe–ZnS nanocrystals.

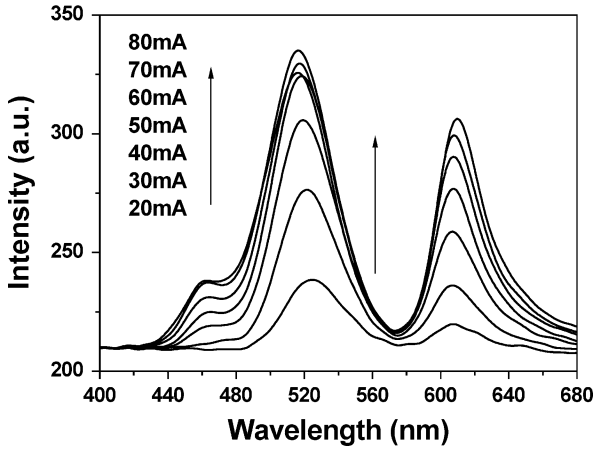

Fig. 5. Room-temperature EL spectra of white light device after nanocrystal coating at various injection current levels.

around 15 nm. At low injection levels, the green intensity is higher than the blue one. As the injection current increases, the blue peak becomes dominating. This trend is attributed to the short migration distance of holes in nitride compounds [3]. At the low injection levels, holes can migrate mainly down to the first QW, which emits green light. Therefore, green emission dominates. As the injection current increases, holes can reach the two middle QWs, which emit blue light. The higher crystalline quality of these two QWs results in the stronger EL peak. The bottom green-emitting QW does not seem to directly contribute much in either PL or EL. This QW was designed for absorbing the down-propagating blue light and then re-emitting green light. However, it is difficult to calibrate its contribution.

Although the comparisons are difficult and dependent on the process conditions, from the current–voltage measurements, we observe that generally the turn-on voltage and the device resistance of the two-wavelength LED lie between the corresponding values of a purely blue and a purely green LED. Nevertheless, this letter means to present the novel concept of white light generation. The details of the blue/green two-wavelength LED will be discussed elsewhere.

We then spin-coated CdSe–ZnS nanocrystals on the fabricated two-wavelength LED. The diameter of the CdSe core is around 4 nm and the thickness of the ZnS shell is about 0.2 nm. The weight concentration of the used nanocrystal toluene solution is 5 Wt/%. Fig. 4 shows the room-temperature PL and photoluminescence excitation (PLE detected at 580 nm) spectra of the nanocrystals. One can see the strong absorption in the shallow UV range. Also, there is an absorption shoulder around 460 nm in the PLE spectrum, which was utilized for blue absorption and red light generation. In the PL spectrum of the nanocrystals, a major peak around 615 nm and a secondary peak around 580 nm can be seen. The room-temperature EL spectra at various injection currents of the LED coated with the nanocrystals are shown in Fig. 5. Here, one can see that the original blue peak is tremendously suppressed and a strong red peak around 615 nm appears. Only the first quantum dot states were excited in our LED operation. The suppression of blue light is due to the conversion of blue photons into red light through the CdSe–ZnS nanocrystals. It can also be attributed to the stronger scattering, when compared with the green light, by the nanocrystals.

In summary, we have grown and processed a blue/green two-wavelength LED based on the mixture of two kinds of QW in epitaxial growth. The relative EL intensity of the two colors depended on the injection current level, which controlled the hole concentration distribution among the QWs. We then coated CdSe–ZnS nanocrystals on the top of the two-wavelength LED for converting blue photons into red light. By coating such nanocrystals, the device emitted blue, green, and red lights for white light generation.

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