Full-color electroluminescence from ZnO-based heterojunction diodes

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Red, green, and blue electroluminescence have been observed from ZnO-based heterojunction diodes consisting of n -ZnO/ n -Mg_yZn_{1-y}O/ Zn_{1-x} Cd_xO/ p -SiC layers. The heterostructures were grown by remote-plasma-enhanced metal-organic chemical vapor deposition. The rectifying I - V characteristics at room temperature reveal the red, green, and blue wavelengths near 720, 520, and 480 nm, respectively, when the diodes are forward biased. It is observed that the emission color can be controlled by changing the cadmium content in the emission layer. © 2007 American Institute of Physics. [DOI: 10.1063/1.2709913]

Wide band gap semiconductors have attracted much attention for light emitting devices in short visible wavelengths.¹ ZnO-based heterostructures are potential candidates for applications in ultraviolet-visible range, over the GaN-based material systems.² ZnO has unique properties such as a wide direct band gap of 3.3 eV and a large exciton binding energy of 60 meV. By doping with MgO or CdO, band gaps of ZnO system can be modulated to the higher or the lower energy level.³ In particular, Zn_{1-x} Cd_xO is regarded as an ideal material having energy level in the whole visible emission range from 3.3 to 1.8 eV.⁴

Several attempts have been made on the development of p -type ZnO and its p - n junctions.⁵⁻⁸ However, reproducible and high quality p -type ZnO material has not been developed and hence ZnO-based p - n junction device is not available. p -type 4H-SiC is a suitable candidate for the p -type conductive substrate as a barrier layer for the ZnO-based device, since it has wurtzite crystal structure and relatively good lattice matching to ZnO with a lattice mismatch of 0.5%. Also 4H-SiC substrates are commercially available. In this letter, we report on the growth and device properties of n -ZnO/ n -Mg_yZn_{1-y}O/ Zn_{1-x} Cd_xO/ p -SiC heterojunction light emitting diodes (LEDs) for the visible full-color light emitting devices. The red-, green-, and blue-color electroluminescence were observed at room temperature.

A schematic diagram of the ZnO-based heterojunction LED prepared by remote-plasma-enhanced metal-organic chemical vapor deposition (RPE-MOCVD) is shown in Fig. 1. Diethyl zinc, dimethyl cadmium, bis(ethylcyclopentadienyl)magnesium and oxygen gas were used as source materials. Details of RPE-MOCVD system and growth aspects are described in our previous reports.^{9,10} Commercial p -type 4H-SiC (0001) wafers ($N_a=2.5 \times 10^{18} \text{ cm}^{-3}$) were used as substrates. The substrates were cleaned in organic solvents followed by an immersion in dilute hydrofluoric acid. The substrate was preheated in a stream of H₂ at 800 °C for 30 min, on which a 200-nm-thick Zn_{1-x} Cd_xO layer was grown at 450 °C. The Zn_{1-x} Cd_xO layers were grown for $x=0.58$, 0.17, and 0.07, having spectral range in red, green and blue (RGB), respectively. This was followed by the

growth of 400-nm-thick Mg_yZn_{1-y}O epilayer as a barrier layer. The electrical properties of n -Mg_yZn_{1-y}O film were examined at room temperature by Hall effect measurements using the van der Pauw configuration. The electron carrier concentration of the nonintentionally doped n -Mg_{0.04}Zn_{0.96}O film was $5.0 \times 10^{19} \text{ cm}^{-3}$. After the growth of Mg_{0.04}Zn_{0.96}O layer, 10-nm-thick n -ZnO with electron concentration of $5 \times 10^{18} \text{ cm}^{-3}$ was grown for the n -type contact layer.

The heterojunction ZnO-based LEDs with dimension of $6 \times 6 \text{ mm}^2$ were fabricated using 10% HNO₃ aqueous solution to etch out the oxide layers to expose the edge of the SiC substrate. Ohmic contacts to the n -ZnO were made of indium (100 nm), which was deposited by the thermal evaporation. The backside contact was formed with 100 nm Au layer.

The typical current-voltage (I - V) characteristics of ZnO-based heterojunction diodes are shown in Fig. 2. The forward and the reverse I - V characteristics show a rectifying behavior with a threshold of 5.6 V at room temperature. The threshold voltage is higher than the band gap of Zn_{1-x} Cd_xO or Mg_{0.04}Zn_{0.96}O, owing to the contact resistance between the p -SiC and gold electrode. The leakage current of $6 \times 10^{-5} \text{ A}$ at the reverse bias with -10 V seems to be relatively large, because the electrode contact area of the diodes is considerably large as $6 \times 6 \text{ mm}^2$. At 6.8 V forward bias, the injection current reaches 40 mA.

Electroluminescence (EL) spectra measured at room temperature for the RGB diodes with the current of 150–200 mA are shown in Fig. 3. The photographs shown in

FIG. 1. Cross-sectional view shows the structure of heterojunction grown on p -SiC substrate.

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FIG. 2. Current-voltage characteristics of heterojunction diode.

Figs. 4(a)–4(c) indicate the electroluminescence images of blue, green, and red emissions in dark, respectively. The emission band with peaks at 480, 520, and 700 nm, respectively, originate from the near interband transitions in $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ active region near the p -SiC interface. It appears that the emission intensities depend on the energy discontinuities between the p -SiC and the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ layers or between the n - $\text{Mg}_{0.04}\text{Zn}_{0.96}\text{O}$ layer and the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ layers. The energy band diagram of n - $\text{Mg}_{0.04}\text{Zn}_{0.96}\text{O}/\text{Zn}_{0.42}\text{Cd}_{0.58}\text{O}/p$ -SiC is presented in Fig. 5. The band gaps of the active layer for cadmium contents $x = 0.07, 0.17$, and 0.58 are 3.0, 2.8, and 2.0 eV, respectively. The electron affinity of $4H$ -SiC is 3.8 eV.¹¹ The electron affinity of $\text{Mg}_{0.04}\text{Zn}_{0.96}\text{O}$ is assumed to be linearly dependent on the magnesium content and lies between 1.7 eV for MgO and 4.3 eV (Ref. 7) for ZnO, giving 4.0 eV for $\text{Mg}_{0.04}\text{Zn}_{0.96}\text{O}$. In the case of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$, the electron affinity is also assumed to be linearly dependent on x and lies between 4.3 eV (ZnO) and 4.5 eV (CdO),¹² leading to 4.4 eV for $x = 0.58$. The energetic barrier ΔE_{C1} for electrons is

$$\Delta E_{C1} = \chi_{\text{ZnCdO}} - \chi_{\text{SiC}} = (4.4 - 3.8) \text{ eV} = 0.6 \text{ eV},$$

while the energetic barrier ΔE_{V1} for holes is

$$\Delta E_{V1} = E_{g,\text{ZnCdO}} + \Delta E_{C1} - E_{g,\text{SiC}} = (2.0 + 0.6 - 3.3) \text{ eV} = -0.7 \text{ eV}.$$

The energetic barrier ΔE_{C2} for electrons is

FIG. 3. (Color online) Normalized electroluminescence spectra of RGB diodes at room temperature.

FIG. 4. (Color online) [(a), (b), and (c)] Photographs of the ZnO-based heterojunction LED sample and the emission of blue, green, and red, respectively, at room temperature.

$$\Delta E_{C2} = \chi_{\text{MgZnO}} - \chi_{\text{ZnCdO}} = (4.0 - 4.4) \text{ eV} = -0.4 \text{ eV},$$

while the energetic barrier ΔE_{V2} for holes is

$$\Delta E_{V2} = E_{g,\text{MgZnO}} + \Delta E_{C2} - E_{g,\text{ZnCdO}} = (3.5 - 0.4 - 2.0) \text{ eV} = 1.1 \text{ eV}.$$

In the case of blue emitting diode, which has 3.0 eV as the band gap of the active layer, the valence band discontinuity ΔE_{V1} shows a negative value, having a type II band alignment. One possibility is that the radiative transition of the blue LED takes place in the interface between the conduction band of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ and the valence band of p -SiC. The EL intensity of the blue LED was 35 times lower than that of the red LED. Even though the EL emission was broad, the emission color was controlled by changing the cadmium content in the active layer. The radiative mechanism can be mainly due to the recombination of the near interface transition at the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ active region near the p -SiC interface.

In summary, we have presented the results of n -ZnO/ n - $\text{Mg}_y\text{Zn}_{1-y}\text{O}/\text{Zn}_{1-x}\text{Cd}_x\text{O}/p$ -SiC heterojunction LEDs fabricated by RPE-MOCVD. The EL transitions were observed from the p - n device at room temperature. These results on the demonstration of ZnO-based full-color visible light emitting diodes show the potential for optoelectronic applications in ultraviolet-visible spectral range.

FIG. 5. Anderson model energy band diagram of n - $\text{Mg}_{0.04}\text{Zn}_{0.96}\text{O}/\text{Zn}_{0.42}\text{Cd}_{0.58}\text{O}/p$ -SiC heterojunction.

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