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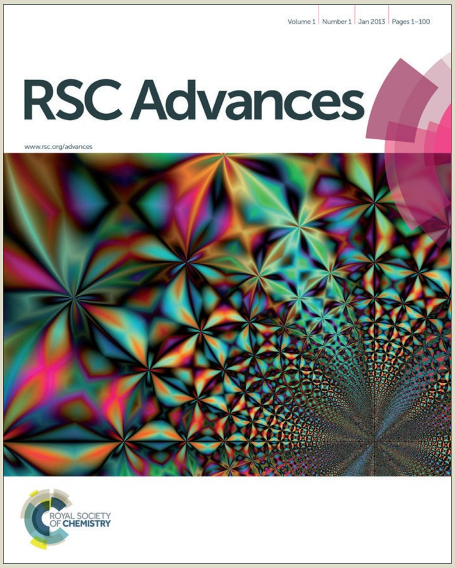

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Multicolour electroluminescence from light emitting diode based on ZnO:Cu/p-GaN heterojunction at positive and reverse bias voltage

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Incorporation of Cu atoms in ZnO can arouse Cu-related defect, which will influence electroluminescence (EL) light of light emitting diode (LED) based on ZnO:Cu/p-GaN heterojunction. ZnO:Cu nanobushes were grown on p-GaN film by simple chemical vapour deposition (CVD) method. Ultraviolet (UV) photoluminescence (PL) peak of ZnO:Cu had a redshift compared with that of pure ZnO, and low temperature (5 K) PL spectrum exhibited a structured green emission, indicating the substitutional incorporation of Cu atoms in ZnO crystal lattice. The LED based on ZnO:Cu/p-GaN heterojunction emitted blue-greenish EL light at p-GaN site at the positive bias voltage, and green EL peak gradually overtook the blue EL peak with the increase of positive bias voltage. At reverse bias voltage, this LED not only exhibited yellow-green EL light at ZnO:Cu site, but also emitted from orange to yellow EL light at p-GaN site with the increase of reverse bias voltage. The origins of EL light at positive and reverse bias voltage were explained using PL spectra and energy band diagram of ZnO:Cu/p-GaN structure.

1. Introduction

Due to the wide direct band gap (3.37 eV) and large exciton binding energy (60 meV)[1] of ZnO, it is considered as one of the most promising materials in high efficient ultraviolet (UV) light emitting diode (LED) at room temperature (RT). ZnO has n-type characteristic because of its self-compensation of native point defects such as oxygen vacancy (V_O) or zinc interstitial (Zn_i). However, the lack of reproducible and high-quality p-type ZnO material restricts the development of ZnO-based p-n homojunction LED. Some p-type semiconductors such as GaN, SiC and $CuAlO_2$ are utilized to construct ZnO-based p-n heterojunction LED.[2-4] In those p-type semiconductors, the band gap energy of GaN (3.40 eV) is similar to that of ZnO (3.37 eV). Moreover, GaN and ZnO have the same wurtzite crystal structure and stacking sequence (2H), and they also possess low lattice mismatch (1.9%)[5]. Thus, p-type GaN is suitable to construct the ZnO-based heterojunction LED.

The LED based on pure ZnO/p-GaN heterojunction usually emits UV or/and blue light.[2,5] Doping with selective elements is a common method, which can manipulate the defects in ZnO to adjust the electronic and optical properties of ZnO-based LED. Actually, the band gap of ZnO can be tuned by doping Ga in ZnO, so the LED based on $Ga_xZn_{1-x}O$/p-GaN can emit from UV (382 nm) to visible (478 nm) light by changing the content of doped Ga.[6] Transition metal Cu is adjacent with Zn element in the periodic table of elements and has the similar ionic radii sizes and configurations of outer electron shells with Zn. Cu is a prominent luminescence activator in II-VI compounds.[7] So Cu is one of the preferable dopant to tune electronic and optical property of ZnO. The incorporation of Cu atoms in ZnO can narrow the bandgap of ZnO, and electroluminescence (EL) emission of Cu-doped ZnO/p-GaN LEDs shifted from UV to violet-blue spectral region compared to pure ZnO/p-GaN LEDs.[8] In addition, Cu dopant arouses deep level defect state in the band gap of ZnO, which is considered to be responsible for green photoluminescence (PL) emission in ZnO.[9-11] Dingle[9] suggested that deep level defect in Cu doped ZnO is due to the charge transfer between Cu^{2+} ions and adjacent oxygen atoms (hole transfers from *d* shell to sp^3 orbitals). Graces[10] claimed that Cu in ZnO may exist in Cu^+ or Cu^{2+} state, and aroused not only unstructured green PL emission by donor-acceptor pair recombination involving the Cu^+ acceptors, but also structured green PL emission related to Cu^{2+} ions. Cu dopant in ZnO will also influence EL light of ZnO-based LED. LEDs based on Cu doped ZnO/p-GaN heterojunction were fabricated using different methods such as thermal diffusion[8], filtered cathodic vacuum arc[12], electrodeposition[13-15], hydrothermal method[16,17]. The formation energy of the group-IB element Cu in ZnO is low under the O-rich condition.[18,19] Therefore, ZnO:Cu nanobushes were grown on p-GaN film by simple chemical vapour deposition (CVD) method under the O-rich condition in this study. The LED based on ZnO:Cu/p-GaN heterojunction emitted multicolour EL lights at different positive and reverse bias voltage. At the positive bias voltage, this LED emitted blue-greenish electroluminescence (EL) light at p-GaN site. At reverse bias voltage, this LED not only exhibited yellow-green EL light at ZnO:Cu site, but also emitted from orange to yellow EL light at p-GaN site with the increase of reverse bias voltage.

2. Experimental Details

2.1 Fabrication of materials

ZnO:Cu nanobushes were fabricated on a commercial p-GaN:Mg film with a sapphire substrate in a horizontal tube furnace by CVD method under O-rich condition. Firstly, the p-GaN:Mg film was coated with a layer of Au thin film of 3-5 nm by magnetron sputtering technology. Next, source material that contained a spot of CuO powder and a mixture of ZnO and graphite powder (weight ratio 1:1) was loaded into a quartz boat. The Au-coated substrate was downstream, close to this quartz boat in a small quartz tube, which was then inserted into the furnace quartz tube. The center position of the source materials in quartz boat was aligned with heating zone of the furnace tube. After a mixture gas contained argon gas of 100 sccm and oxygen gas of 3 sccm passed through the furnace tube, the pressure of the furnace tube was maintained at the 7×10^3 Pa by adjusting release valve of tube furnace. At last, the reaction was carried out at 950℃ for 20 minutes. When the furnace cooled to RT, gray-colored products of ZnO:Cu were grown on the p-GaN film. Pure ZnO was fabricated by the same procedure without adding CuO in source material.

2.2 Characterization

The morphology of ZnO:Cu was characterized by a high-resolution field emission scanning electron microscope (SEM) (FEI Nova Nano-SEM 450). X-ray diffraction (XRD) of ZnO:Cu was carried out using a Rigaku x-ray diffractometer with Cu Kα radiation and Ni filter. Chemical analysis of ZnO:Cu was performed by x-ray photo spectrometry (XPS) using a Riber LAS-3000 instrument with a Mg Kα x-ray source having an energy resolution of 0.9-1.0 eV (VGMultilab 2000). The samples PL measurements were executed at RT using a He-Cd laser line of 325 nm with the power of 30 W as the excitation source (Horiba Jobin Yvon, Lab RAM HR800). The PL measurements at low temperature of 5 K were performed by the Ti:sapphire femtosecond laser (Coherent Mira 900) (exciting wavelength of 350 nm) with an excitation power of 0.20 mW in superconducting magnet cryostat (OXFORD Microstate MO) and analysed using monochromator (Shamrock 500i) with EMCCD (Newton 970) under the environment of liquid helium. The electrical properties of the as-prepared LED device were tested using a two-probe station with Keithley 4200 semiconductor parameter analyzer at RT. The EL spectrum of the as-fabricated LED was collected by a high-sensitivity fiber optic spectrometer equipped with a cooled charge-coupled device detector (AvaSpec-HS1024×122TEC-USB2).

3. Results and discussion

The oblique-view SEM image of ZnO:Cu on p-GaN film exhibits morphology of the decussate nanobushes, as shown in Fig. 1a. It is obvious that the decussate nanobushes structure introduced surface roughness, which can scatter light and be beneficial to enhance light extraction efficiency, similar to GaN-based LED with etched nano-rough surface[20]. To figure out whether doping Cu in ZnO changed ZnO crystal lattice, the XRD spectra of pure ZnO and ZnO:Cu were executed, as depicted in Fig. 1b. All peaks of ZnO:Cu can be indexed as hexagonal wurtzite ZnO structure (JCPDS 36-1451, $P6_3mc$). No trace of any secondary phases (such as CuO and Cu_2O) was found within the sensitivity of XRD measurements compared with that of pure ZnO. This means that the dopant Cu did not change significantly the wurtzite structure of ZnO. The XPS measure was also performed to identify existence and valence state of Cu in ZnO:Cu, as shown in Fig. 1c. The survey spectrum of XPS reveals the presence of Cu, Zn and O. A high resolution scan spectrum of the Cu2p peaks in the inset of Fig. 1c was obtained, which shows a broad satellite peak and a prominent peak located at 932.7 eV corresponding to $Cu2p_{3/2}$ spin-orbit splitting. The dominated peak curve can be Gaussian fitted with a major Cu^+ component (by fixing $2p_{3/2}$ peak at 932.6 eV) and a Cu^{2+} minor component (by fixing $2p_{3/2}$ peak at 933.6 eV). In addition, the satellite peak resulted from electron shakeup in Cu3d band ($Cu3d^9$ configuration) of the cupric oxide (Cu^{2+}) with hole

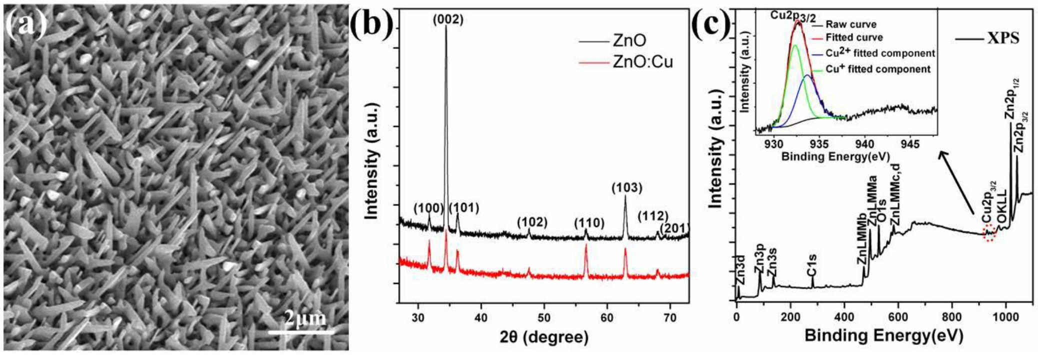

Fig. 1 (a) 30° oblique-view SEM image of decussate ZnO:Cu nanobushes on p-GaN film. (b) XRD comparison of pure ZnO and ZnO:Cu on p-GaN film with sapphire substrate. (c) XPS survey spectrum of ZnO:Cu/p-GaN structure. High resolution scan spectrum of XPS spectrum for Cu 2p peaks is shown in the inset of (c).

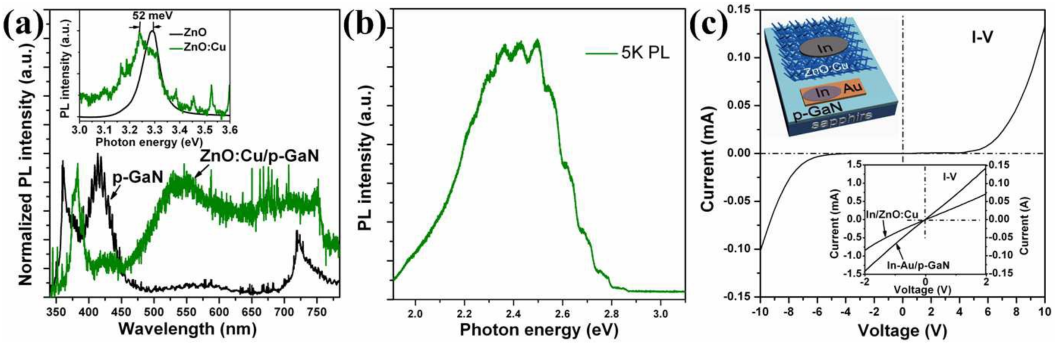

Fig. 2 (a) RT PL spectrum of ZnO:Cu/p-GaN structure and p-GaN film. Comparison of undoped ZnO, ZnO:Cu/p-GaN RT normalized PL spectra is shown in the inset of (a). (b) Low temperature (5 K) PL spectrum in green region of ZnO:Cu/p-GaN structure. (c) I–V characteristics of this ZnO:Cu/p-GaN heterojunction LED at RT. Schematic diagram of the ZnO:Cu/n-GaN LED device is shown in the upper inset of (c), and the characterization of Ohmic contacts on each part is shown in the lower inset of (c).

states[21] is simultaneously found in the binding energy range of 938-945 eV. So Cu exhibited a mixed valence state of Cu$^+$ and Cu^{2+} in ZnO.

The PL measurements of pure ZnO and ZnO:Cu on p-GaN film, and p-GaN film at RT were measured, respectively. The PL spectra of ZnO:Cu/p-GaN structure and p-GaN film were shown in Fig. 2a. The band edge emission of about 365 nm in the PL spectrum of p-GaN film is attributed to the exciton recombination, and the blue emission peak ascribe to the transition between the conduction band and deep Mg-dopant induced acceptor levels[22] in p-GaN. And a near-band-edge emission of 383 nm and a defect related visible band emission in region from green to red can be observed in the spectrum of ZnO:Cu/p-GaN structure. In addition, the normalized PL spectra of the pure ZnO and ZnO:Cu at higher energy are presented in the inset of Fig. 2a. The UV peak of ZnO:Cu (383 nm, 3.237 eV) had a red-shift of ~52 meV compared with that of pure ZnO (377 nm, 3.289 eV). This red-shift phenomenon of UV PL peak was attributed to the coupling between the band electrons and the localized Cu^{2+} impurity spin[23], which reduced bandgap of ZnO. And the red-shift also indicated that Cu partially substituted for Zn atoms in the ZnO crystal lattice. On the other hand, the visible emissions from green to red in the ZnO:Cu/p-GaN structure is the result that Cu doping in ZnO aroused much more intrinsic and extrinsic defects.[8] Visible PL light are related to deep level energy emission, which probably originated from the extrinsic defect from Cu dopant and the intrinsic defects of Zn$_i$, V$_O$, zinc vacancy (V$_{Zn}$), and oxygen interstitial (O$_i$).[9-11,24,25] According to the prior literatures[11,24,25], the Cu dopants at Zn sites can result in the green PL emission[11], and the O$_i$ defect can lead to the orange-yellow broad PL emission[24]. In addition, the red PL emission can be ascribed to the band transition from the V$_O$ energy level to the top of the valence band in ZnO:Cu.[25] Moreover, structured green emission in low temperature PL spectrum is typical characteristic in ZnO containing Cu.[9-11] So PL spectrum of ZnO:Cu in green region was also measured in low temperature (5K), as shown in Fig. 2b. The structured green PL emission with an LO-phonon energy interval of ~72 meV for ZnO was observed, which can be attributed to a localized excitation of a Cu^{2+} ion at zinc site.[26] The occurrence of structured green PL emission further verified the substitutional Cu ion at zinc site in ZnO.

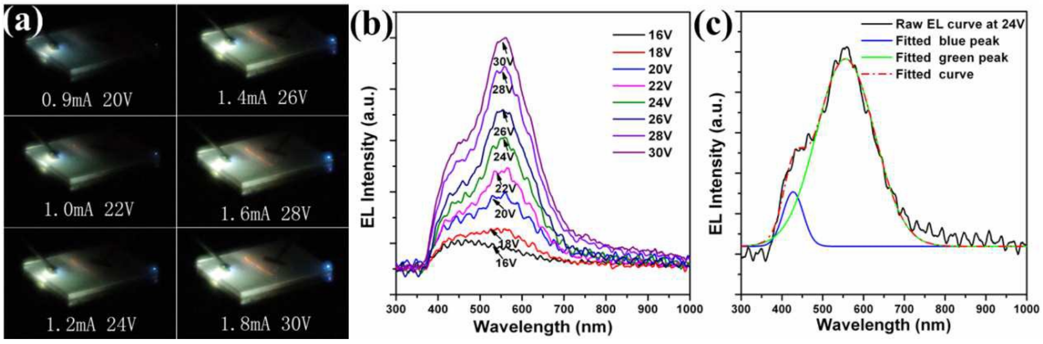

Fig. 3 (a) Photo galleries of RT EL emission from p-ZnO:Cu/p-GaN LED at positive bias voltages from 20 V to 30 V. (b) EL spectra at p-GaN site (left) at different positive bias voltages from 16 V to 30 V. (c) Gaussian fitted EL spectrum at positive bias voltage of 24 V with blue peak at 414 nm and green peak at 556nm.

A schematic diagram of the ZnO:Cu/p-GaN LED device is shown in the upper inset of Fig. 2c. Au film of 10 nm thick was thermally evaporated on p-GaN part through mask. The Au layer was contacted with metal indium (In) in order to form Ohmic contact with the p-GaN film. Metal In was directly contacted with

ZnO:Cu. From the linear I-V Curves in the lower inset of Fig. 2c, it is deduced that Ohmic contacts on each part were achieved. Fig. 2c shows I-V characteristics of the fabricated Cu:ZnO/p-GaN structure measured at RT with p-GaN as the positive pole through a two-probe station. The non-linear I-V curve exhibits rectifying diode-like behaviour, which bespeaks possibility of light emission.

The EL spectra from ZnO:Cu/p-GaN LED device were measured at various positive and reverse bias voltages with a direct current source meter at RT. A high-sensitivity fibre optic spectrometer collected EL light of this LED. The photos of EL light at positive bias voltages from 20 V to 30 V are shown in Fig. 3a. The blue-greenish EL light came from p-GaN site (right side) and could be observed with the naked eye in a dark environment. However, no EL emission light was detected at ZnO:Cu site (left side). The EL spectra in p-GaN region at different positive bias voltages are shown in Fig. 3b. Fig. 3c shows EL spectrum at positive bias voltage of 24 V which was Gaussian fitted with blue peak at 414 nm and green peak at 556 nm. From Fig. 3b, we observed that the intensity of main emission in EL spectra increased and intensity of green EL gradually overtook blue EL with the elevation of positive bias voltage. No obvious shift of peak location was observed in EL spectra.

When reverse bias voltages were applied on this LED device, the ZnO:Cu/p-GaN region emitted yellow-green light. Meanwhile, p-GaN site emitted from orange to yellow light with the elevation of reverse bias voltage. This phenomenon can be observed from the photos of EL light at reverse bias voltages from 20 V to 30 V in Fig. 4a. The corresponding EL spectra were shown in Fig. 4b and Fig. 4c, respectively. Obviously, the light emission behaviours at reverse bias voltages are different from that at forward biased voltages. The EL light from p-GaN site changed from orange to yellow and blue-shifted from 651.6 nm to 613.5 nm with the elevation of reverse bias voltage. The yellow-green EL peak from ZnO:Cu site at positive bias voltage of 30 V was divided into two peaks. One is corresponding to the EL fitted peak from p-GaN site at the same reverse bias voltage, and the other divided peak will be centred at around 550 nm. The same fitting procedures of EL curves at reverse bias voltage from 22 V to 30 V were also performed. It is found that the divided peak at around 550 nm always remains constant.

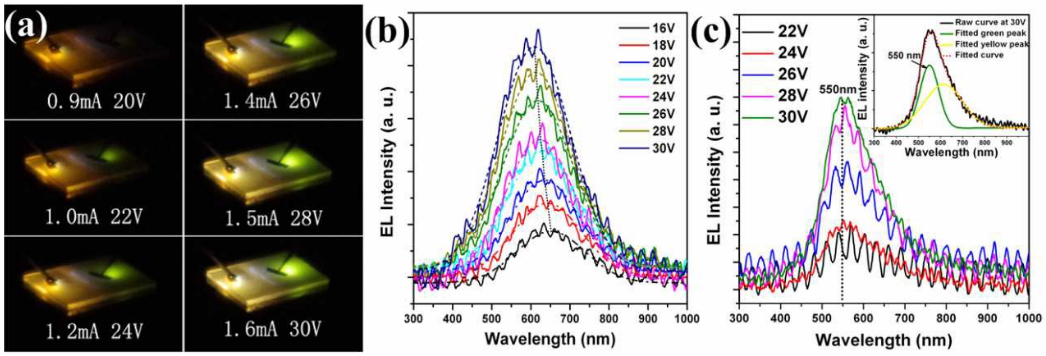

Fig. 4 (a) Photo galleries of RT EL emission from p-ZnO:Cu/p-GaN LED at reverse bias voltage from 20 V to 30 V. (b) EL spectra at p-GaN site (left) at different reverse bias voltages. (c) EL spectra at ZnO:Cu/p-GN site (right) site at different reverse bias voltages from 22 V to 30 V. Gaussian fitted EL spectrum at reverse bias voltage of 30 V, with blue peak at 414 nm and green peak at 556 nm.

In order to account for the origin of EL peak at positive and reverse bias voltages, energy band diagram of ZnO:Cu/p-GaN heterojunction is illustrated in Fig. 5a, which exhibits type II band alignment with an interface configuration-dependent valence band offset having an average value of 1.6 eV[27]. Energy band diagram of ZnO:Cu/p-GaN heterojunction at positive bias voltages is described in Fig. 5b. Electrons from the conduction band of ZnO:Cu arrived at the ZnO:Cu/GaN interface and were captured by the deep-level states near the interface such as V_O or/and Cu induced deep level[28], thus yielding green band around 556 nm. The carrier mobility of electron in the ZnO:Cu is higher than that of the p-GaN due to the difference in the effective mass and carrier scattering mechanism. Electrons could not be completely blocked in the ZnO:Cu region and will pass through the interface. Some of the electrons in ZnO:Cu will inject into the p-GaN site to recombine with deep Mg acceptor level defects in p-GaN which leads to blue emission at p-GaN site[29], corresponding with the blue peak in PL spectrum of p-GaN. When the applied positive voltage increased, more electrons arrived at ZnO/GaN interface and recombination at the interface increased more rapidly, overtook the recombination between electron that passed through the interface and deep Mg acceptor level defects in p-GaN. It is consistent with the EL spectra in p-GaN region at different positive bias voltages. Fig. 5c described energy band diagram of ZnO:Cu/p-GaN heterojunction at reverse bias voltages. When reverse bias voltage was applied on this heterojunction, the thickness of tunnelling barrier became very thin either by lowering the ZnO

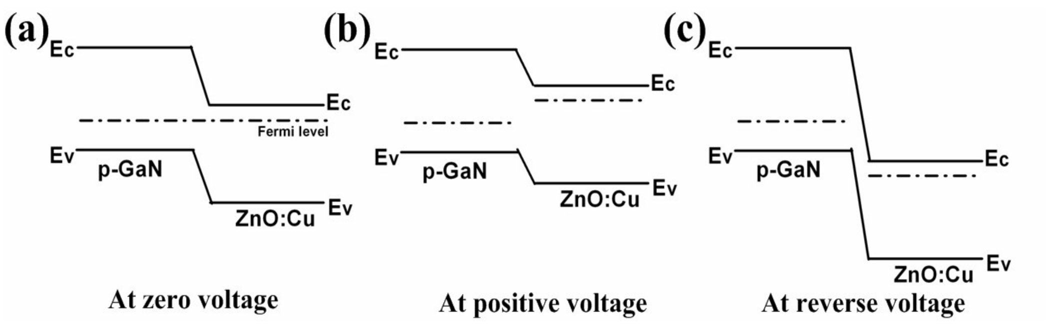

Fig. 5 Band diagram of the ZnO:Cu/p-GaN heterojunction (a) at zero voltage. (b) at positive bias voltage. (c) at reverse bias voltage.

conduction band or by raising the valence band of GaN as a result of large band offset. The occupied states of the valence band of p-GaN would be higher than the unoccupied states of the conduction band of ZnO:Cu, which will results in the movement of electrons toward lower energy than the recombination with acceptors in the valence band of GaN. Thus blue light related with the transition from the conductive band to deep Mg acceptor level defects in p-GaN will not appear. The recombination related with electron that tunnelled from p-GaN to ZnO:Cu will occur at the ZnO:Cu site, and stable green emission light of 550 nm resulting from substitutional Cu$^+$ and Cu^{2+} at zinc site[10] would be emitted. It is also consistent with the PL green peak of ZnO:Cu/p-GaN structure. For EL light from p-GaN site, blue-shifted from 651.6 nm to 613.5 nm with the elevation of reverse bias voltage, which was also contained in yellow-green EL light at ZnO:Cu site. So it is considered as the interface recombination radiation in ZnO:Cu/p-GaN interface. Kishwar[30] considered that a broad orange-red EL band centred at 650 nm is associated with the transition from the conduction band of ZnO to O$_i$ combined with recombination from Zni to O$_i$ in ZnO/p-GaN LED. Based on this case, the increase of the reverse bias voltage further lower the ZnO conduction band or raised the valence band of GaN, the electron which tunneled from p-GaN to ZnO:Cu may possess higher energy[31], thus the recombination of the electrons in the conduction band of ZnO with O$_i$ acceptor level produce photons with relatively higher energy, leading to a continuous blue shift of the EL emission peak in ZnO:Cu/p-GaN interface from orange to yellow.

4. Conclusion

In summary, ZnO:Cu nanobushes were grown on p-GaN film by CVD method and the LED based on ZnO:Cu/p-GaN heterojunction emitted multicolour EL light at positive and reverse bias voltage. Among them, this LED based on ZnO:Cu/p-GaN heterojunction emitted blue-greenish EL light at p-GaN site at positive bias voltage. At reverse bias voltage, this LED not only exhibited yellow-green EL light at ZnO:Cu site, but also emitted from orange to yellow EL light at p-GaN site with the increase of reverse bias voltage. Visible EL light induced by Cu-related defect in ZnO:Cu/p-GaN LED is valuable in fabricating practical visible LED in real life.

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Notes and References

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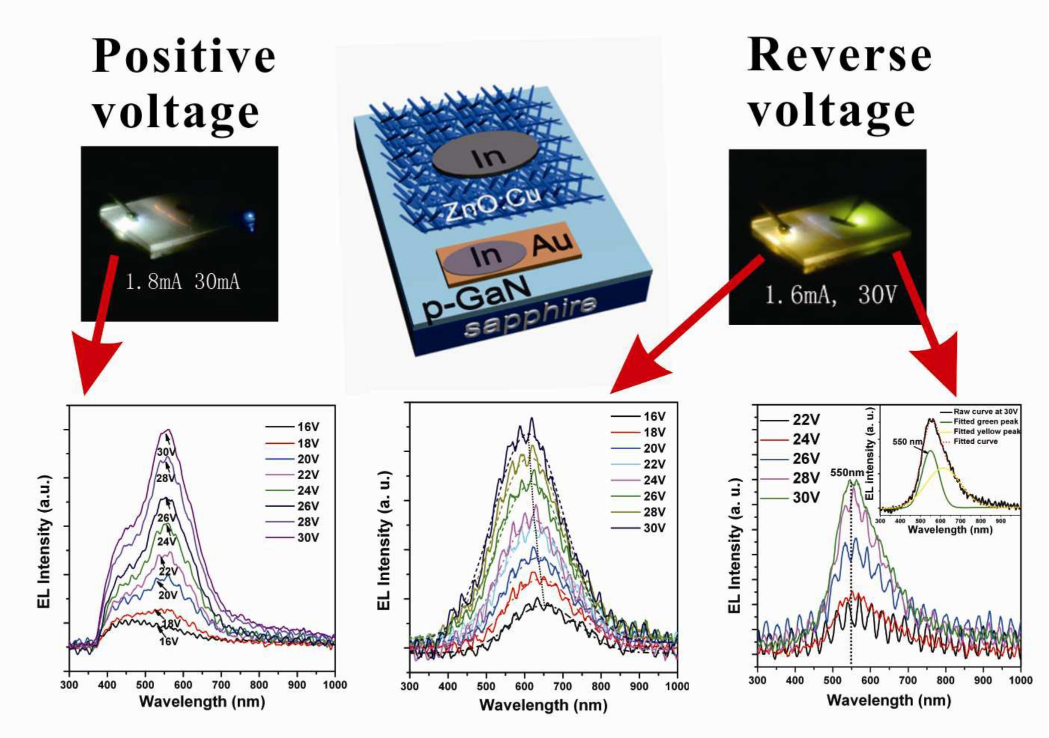

The ZnO:Cu/p-GaN LED made by simply CVD method emitted different multicolour EL light at positive and reverse bias voltage.