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Dual electroluminescence from hybrid p-n junction LEDs composed of oxide and organic semiconductors

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1. Introduction

We fabricated hybrid p-n junction light-emitting diodes (LEDs) using room temperature sputtered ZnO and N,N′-diphenyl-N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD), in which the ZnO and the α-NPD served as n- and p-type component of the junction, respectively. The device shows a current rectifying characteristic similar with conventional p-n junction diodes. The device performance, such as turn on voltage, current density, and electroluminescence (EL) efficiency, is improved by post-deposition annealing. XRD profiles indicate that strain relaxation of as-deposited ZnO films has an important role for the improvements. Different from conventional and other hybrid LEDs, the device exhibits distinct two EL bands in blue and green regime. Room temperature photoluminescence (PL) spectra of the ZnO and α-NPD layer show consistent peak energies with the EL spectra from the hybrid LEDs, implying that the radiative charge recombinations occurs in both components. Because the entire device processes including post-deposition annealing are performed at low temperatures (below 200 ℃), it is reasonable to expect that the fabrication of the device is also compatible with flexible plastic substrates.

2. Experiment

The ZnO and α-NPD films used in this work were prepared without substrate heating. The Al-Si (1:1 wt%) electrode and insulating ZnO films were deposited on Si (001) substrates by rf magnetron sputtering. The chamber was pumped to a pressure of 4×10^{-4} Pa. The targets were pre-sputtered for 10 min. to remove surface impurities and to stabilize the system. Only Ar was used as working gas. The gas flow rate and rf power were maintained at 12 sccm and 50 W, respectively. Under the condition, deposition pressure was 0.8 Pa and the deposition rate 8 nm/min. The deposited films were annealed in vacuum for 120 min at different temperatures 100, 150, and 200 ℃. After optimizing annealing temperature using a 200-nm-thick ZnO film, we varied the ZnO thickness from 100 to 400 nm. The surface morphologies and crystallinities of the as-deposited and annealed ZnO films were characterized by AFM and XRD using Cu $K\alpha_1$ radiation (λ=1.54 Å). Subsequently, 100-nm-thick α-NPD layers were evaporated on these ZnO films with a deposition rate of 0.8 Å /s. Finally, a molybdenum trioxide (MoO_3) layer and an Al electrode (anode) with thicknesses of 5 and 35 nm, respectively, were evaporated through a shadow mask with a dimension of 500 μm×500 μm square. Current-vs-voltage (*I-V*) characteristics of the hybrid LEDs was studied with a Keithley 4200 semiconductor parameter analyzer at room temperature and in nitrogen-filled glove box without exposure to air. Photoluminescence measurements were carried out using a He-Cd laser with 325 nm at room temperature. EL spectra was taken with an Ocean optics spectrometer with a spectral resolution of ~0.3 nm,

3. Results and discussion

In general, ZnO is intrinsically n-type due to the deviation from stoichiometry arising from the presence of O vacancies or Zn interstitials, which forms shallow levels near the conduction band. Therefore, we deposited the ZnO films without O_2 flow to obtain high electron concentration as possible. However, despite the deposition condition, the resistivities of the as-sputtered and annealed ZnO films were too high to be measured by van der Pauw measurement. This implies that the layers have insulating properties. The resistivity of a ZnO film annealed at 150 ℃, as a representative case, was estimated by *I-V* characteristic, revealing a high resistivity of ~8.5 MΩ cm.

I-V curve of the hybrid p-n junction structure exhibits current rectifying behavior, indicating the present of a good p-n junction between the components. The *I-V* characteristics, such as turn-on and current density, were changed remarkably by increasing annealing temperature as shown in Fig. 1.

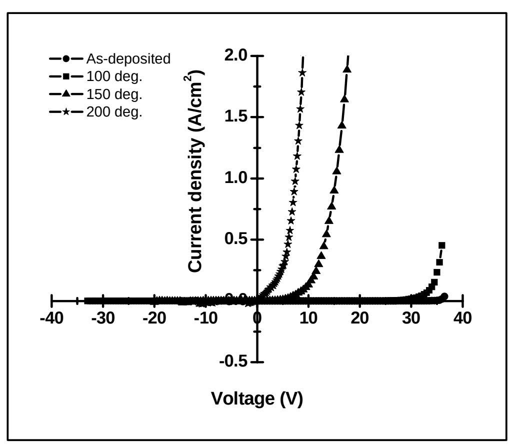

Fig. 1. *I-V* characteristics of the hybrid LEDs depending on annealing temperature of ZnO films.

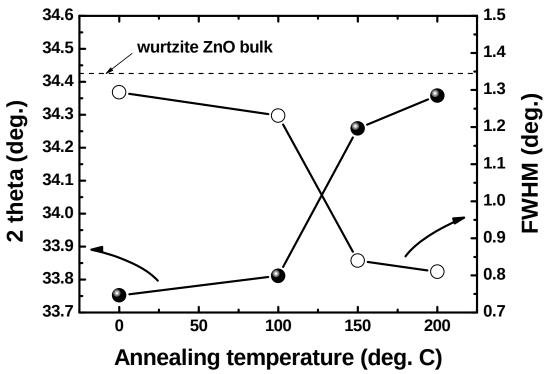

Fig. 2. Variation of diffraction angle and FWHM of ZnO (002) plane depending on annealing temperature.

SEM image of the sputtered ZnO films exhibits columnar grains preferentially oriented along *c*-axis. Consistently, the θ-2θ XRD profile of the as-deposited ZnO film exhibits a peak at 33.75º, corresponding to the (002) plane of Wurtzite ZnO crystal. The ZnO (002) diffraction angle is lower than that of bulk ZnO (2θ=34.43º corresponding to *c*=0.52069 nm), implying the film is under tensile stress along the *c*-axis (i.e., biaxial compressive stress along planar directions). The intrinsic stress in sputtered ZnO films is presumably caused by recoil implantation of the ZnO surface atoms as reported earlier.[1]

As shown in Fig. 2, XRD profiles of the ZnO films indicate that post-deposition annealing lead to a remarkable change in crystallinity. Annealing at 100 ℃ had little effect, whereas, for an annealing temperature of 150℃, the (002) diffraction peak shifts to higher angles and its FWHM also decreases significantly. The (002) diffraction appearing at 34.26º for the ZnO film annealed at 150 ℃ is close to the value of unstressed ZnO, indicating that the stress is almost relaxed. The crystallization process is related to desorption of oxygen rather than Zinc especially for the ZnO film deposited in low pressure. On the other hand, AFM images of the as-deposited and annealed ZnO do not show any significant

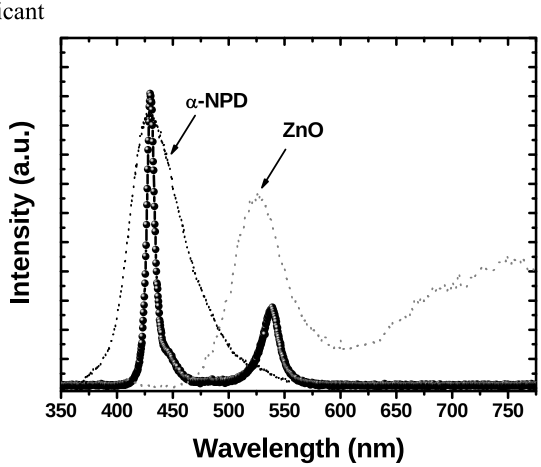

Fig. 3. Room temperature EL (circles) and PL (dotted lines) spectra of the hybrid LED, α-NPD and ZnO.

variations in surface morphology in the annealing temperatures up to 200 ℃.

According to the improvement in crystallinity, the EL from the LEDs was improved by annealing. Good EL intensities are obtained from the LEDs with 200 and 300-nm-thick ZnO films annealed at 150 ℃. The EL spectrum of the device and PL spectra of α-NPD and ZnO films we used are shown in Fig. 3. The result clearly exhibits the EL bands are originated from charge recombination in both ZnO and organic films. Although there are several reports on hybrid LEDs (e.g., ZnO/organic, ZnO/nitrides, and ZnO/oxides), such EL properties have not been reported yet. The previous works pointed out that the band alignment or difference of carrier concentration between the components favors one-sided charge injection from one into another, appearing single EL band.[2,3] Contrast to these works, the dual EL properties of the hybrid LEDs can be explained as a result of effective electron injections from ZnO into α-NPD and hole injection from α-NPD into ZnO under forward bias, then, radiative recombination of injected charges in both components.

3. Conclusions

In conclusion, a hybrid p-n junction LEDs was demonstrated using ZnO and α-NPD. We obtained the current rectifying characteristic similar with inorganic p-n junction structure. Furthermore, the organic material is also severed as light-emitting host together with ZnO. As a result, we obtained blue and green emissions. We expect that the promising features of the hybrid device could provide new routes to fabricating white LEDs, for example, by adding a red fluorescence material to the device structure. It is worth noting that the LEDs were fabricated at low temperatures. Undoubtedly, such low temperature process should be applicable to large area and flexible light-emitting sources.

Acknowledgements

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