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Ultraviolet electroluminescence from n-ZnO:Ga/p-ZnO:N homojunction device on sapphire substrate with p-type ZnO:N layer formed by annealing in N_2O plasma ambient

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ABSTRACT

ZnO homojunction light emitting device (LED) with n-ZnO:Ga/p-ZnO:N structure was fabricated on sapphire substrate by metal organic chemical vapor deposition. The reproducible p-type ZnO:N layer with hole concentration of 1.29×10^{17} cm^{-3} was formed with NH_3 as N doping source followed by thermal annealing in N_2O plasma protective ambient. The device exhibited desirable rectifying behavior. Distinct electroluminescence emission centered at 3.2 eV and 2.4 eV were detected from this device under forward bias at room temperature. The intensive ultraviolet emission was comparable to the visible emission in the electroluminescence spectrum, which represent remarkable progress in the performance of ZnO homojunction LED.

1. Introduction

ZnO has attracted great interest for its wide band gap (3.37 eV) and relatively large exciton binding energy (60 meV) at room temperature. It has been regarded as one of the most promising candidates for the next generation of short-wavelength light emitting diode (LED) and lasing devices [1,2]. However, the realization of stable and reproducible p-type ZnO with acceptable electrical and crystalline properties for optoelectronic devices has long been the bottleneck for ZnO-base materials applications [3]. Nitrogen has been predicted to be the most promising p-type dopants for ZnO [4]. Great efforts had been made to realize ZnO homojunction LED based on p-type nitrogen doped ZnO and some electroluminescence (EL) phenomenon were reported previously [3,5–13]. Nevertheless, the deep level emission was generally overwhelming in the EL spectrum due to the very limited hole concentration and low hall mobility of the p-type ZnO:N layer. It was found that untreated nitrogen doped ZnO sample generally exhibited poor electrical properties and crystalline quality [5–10]. Thermal annealing were usually employed to treat ZnO:N sample since it is an effective technique to improve crystalline quality as well as activate acceptor impurities in ZnO. However, thermal annealing will inevitably resulted in decompose of nitrogen and oxygen from the sample, which will be harmful for the properties of ZnO:N sample [14–16]. To solve this dilemma and exploit the advantage of nitrogen dopant, a potent technique that can effectively restrain decompose of nitrogen and oxygen in annealing process as well as improve the crystalline quality is needed.

In this Letter, a novel technique to realize effective p-type ZnO was developed with ammonia as N doping source followed by thermal annealing in N_2O plasma protective ambient. N_2O plasma can provide both nitrogen ion and oxygen ion, which will be helpful for restrain the decompose of nitrogen and oxygen from ZnO:N sample during thermal annealing process under high temperature. Based on the p-ZnO:N film, ZnO homojunction LED with n-ZnO:Ga/p-ZnO:N structure was fabricated on *c*-plane sapphire substrate by metal organic chemical vapor deposition (MOCVD). Distinct EL emission peaks centered at 3.2 and 2.4 eV were detected from this device under forward bias at room temperature. The intensity ratio of near band edge emission to deep level emission in electroluminescence spectrum was significantly enhanced compared with other ZnO homojunction device on sapphire substrate [5–10]. The results reported here demonstrate that reproducible p-ZnO:N film and ZnO-based LED can be effectively realized by this new processing technique. Furthermore, the realization of UV EL from ZnO p–n junction fabricated by MOCVD technique paves the way for future industrialization.

2. Experiment

A schematic diagram of the ZnO-based homojunction LED structure is shown in Fig. 1. ZnO homojunction was produced on *c*-plane

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sapphire substrate by MOCVD. *c*-Plane sapphire was chosen as substrate because both sapphire and ZnO have the same crystal structure of hexagonal close-packed. Diethylzinc and O_2 were chosen as precursors of Zn and O, respectively. Trimethylgallium and NH_3 were used for n-type and p-type doping respectively. Firstly, a 60 nm ZnO buffer layer was deposited on *c*-plane sapphire substrate at 500 °C. The Ga-doped n-type ZnO with a thickness of 1.5 μm was grown on the buffer layer at 700 °C. For nitrogen doping, NH_3 flux was induced into the chamber and the growth temperature was adjusted to 600 °C. Thickness of the ZnO:N layer was about 500 nm. Then the ZnO sample was *in situ* annealed in N_2O plasma ambient at 800 °C for 40 min. N_2O was activated by a radio frequency source (13.56 MHz) with a power of 200 W. To fabricate the ZnO LED, the top ZnO layer was etched by NH_4Cl aqueous solution by masking the surface, the etch depth was about 600 nm, details about the etching treatment was reported in our previous work [17]. Au–Zn and Au–Ni electrode were deposited on the n-type ZnO and p-type ZnO layer by thermal evaporation technique, respectively. Then the device was annealed in nitrogen atmosphere at 400 °C for 5 min to reduce contact resistance as well as increase adhesive force. As a result, ZnO-based LED was fabricated.

To investigate the properties of the n-type and p-type ZnO layer, individual ZnO films were fabricated under the identical growth condition as mentioned above. The crystalline quality of the ZnO films was determined by X-ray diffraction (Shimadzu XRD-6000 system with Cu Kα radiation $\lambda = 0.15406$ nm). The etching depth was measured by profilometer (T 4000). The electrical properties were measured by Hall system (Bio-Rad HL5500) using Van de Pauw method. To identify the chemical state of the doped nitrogen in the p-type ZnO layers, X-ray photoelectron spectroscopy (XPS) measurement was conducted by VG ESCA LAB MK II. The current–voltage (*I*–*V*) characteristics were measured using a XJ4810 semiconductor diode parameter analyzer at room temperature. The photoluminescence (PL) measurement was carried out by a Jobin Yvon HR320 spectrometer using a He–Cd laser (325 nm, 30 mW). The EL was also measured by HR320 spectrometer. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 2 shows the XRD patterns of ZnO:Ga film and ZnO:N annealed in N_2O plasma ambient. Besides sapphire (006) diffraction peak, only two distinct diffraction peaks corresponded to ZnO (002) and ZnO (004) can be observed from both ZnO:Ga and annealing treated ZnO:N film. The full-width at half-maximum (FWHM) of ZnO (002) peak of ZnO:Ga and annealing treated ZnO:N films are 0.10° and 0.18°, respectively, indicting that the ZnO films are strongly *c*-axis-oriented with high crystalline quality.

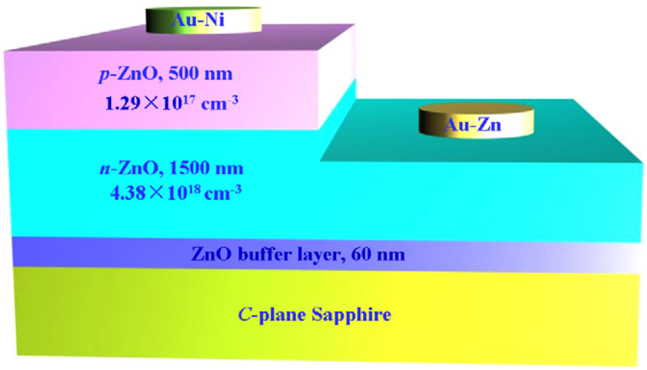

Fig. 1. Schematic diagram of the ZnO-based LED.

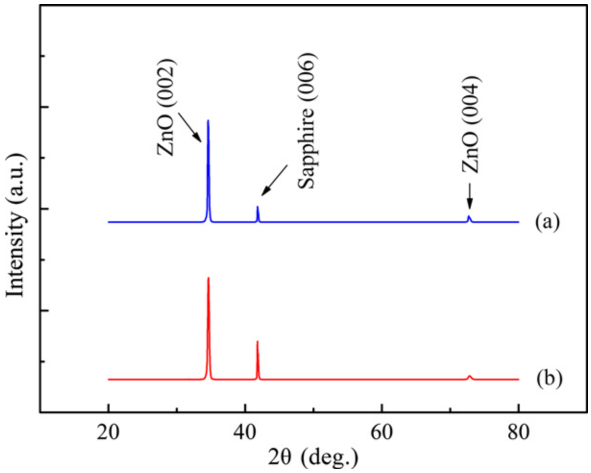

Fig. 2. XRD patterns of ZnO:Ga film and ZnO:N film annealed in N_2O plasma ambient.

Table 1 shows the Hall measurement results of the Ga-doped and ZnO:N individual layers deposited on *c*-plane sapphire. The Ga-doped ZnO film exhibits desirable n-type conductivity of 0.05 Ω cm. The as-deposited ZnO:N film shows high resistivity with low carrier concentration of 8.92×10^{14} cm^{-3} as can be seen in Table 1. ZnO:N film converts to p-type with hole concentration of 1.29×10^{17} cm^{-3} after annealed in N_2O plasma ambient at 800 °C. Meanwhile the mobility of the ZnO:N film increases from 0.79 to 2.15 cm^2 V^{-1} s^{-1}. This indicated that such annealing condition can effectively improve the electrical properties of ZnO:N film. For comparison, the routine N_2 and O_2 were also employed in the annealing process. The results indicated that N_2O plasma exhibited effective improvement on the electrical and crystalline qualities of ZnO:N sample and details will be reported elsewhere.

The XPS measurement results of the nitrogen chemical state in ZnO film is shown in Fig. 3. The spectra shows two N 1s related peaks located at 396.5 and 404.1 eV, respectively. The lower peak centered at 396.5 eV is a typical signal of N–Zn bond, which is helpful for forming acceptor in ZnO film [6,16,18]. The 404.1 eV peak is associated with nitrogen compounds such as N_2O (nitrite). [6,18,19]. After annealing in N_2O plasma ambient at 800 °C, the peak located at 404.1 eV distinctly decreased while the 396.5 eV peak became dominant. The results indicated that the chemical state of N changed considerably and N in ZnO mainly existed as N–Zn bond after annealing [18,19], which should be responsible for the p-type ZnO. Although the influence of nitride related to 404.1 eV on the conducting carrier in ZnO is still unclear [6], we supposed that nitrite may play a negative role for fabricating p-ZnO:N.

Table 1
Electrical properties of ZnO films on *c*-plane sapphire

ZnO samples	Conductivity type	Resistivity (Ω cm)	Hall mobility (cm^2 V^{-1} s^{-1})	Carrier concentration (cm^{-3})
Ga-doped ZnO	n	0.05	28.50	4.38×10^{18}
As-deposited ZnO:N film	Ambiguous	8552.85	0.79	8.92×10^{14}
ZnO:N film then annealed in N_2O plasma at 800 °C	p	22.50	2.15	1.29×10^{17}