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Additional information on Appl. Phys. Lett.

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A ZnO *p-n* junction light-emitting diode (LED) was fabricated on *a*-plane Al_2O_3 substrate by plasma-assisted molecular-beam epitaxy. NO plasma activated by a radio frequency atomic source was used to grow the *p*-type ZnO layer of the LED. The current-voltage measurements at low temperatures showed a typical diode characteristic with a threshold voltage of about 4.0 V under forward bias. With increasing temperature, the rectification characteristic was degraded gradually, and faded away at room temperature. Electroluminescence band of the ZnO *p-n* junction LED was located at the blue-violet region and was weakened significantly with increase of temperature. This thermal quenching of the electroluminescence was attributed to the degradation of the diode characteristic with temperature. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2166686]

After being investigated as a green fluorescence material for many years,[1,2] recently, ZnO has attracted more and more attentions as an ultraviolet light-emitting material.[3,4] As an oxide, ZnO is superior over nitrides in thermal stability as well as in resistance to chemical attack and oxidation. Its large exciton binding energy (60 meV) is in principle favorable to high efficient RT excitonic emission. In order to overcome the "asymmetric doping" limitation, researchers have concentrated on the growth of high quality *p*-type ZnO layers, and have achieved great improvements in the past three years.[5–7] However, only few works on *p-n* ZnO light-emitting diode (LED) have been reported.[8,9] Recently, Tsukazaki *et al.* reported electroluminescence (EL) from a ZnO *p-n* junction,[6,10] which opened a door to realize ZnO-based light-emitting diodes. In those reports, the LEDs were fabricated either on $ScAlMgO_4$, or bulk ZnO substrates.[6,8,10] In this letter, we report blue-violet light emission from a ZnO *p-n* homojunction diode, where the *p*-type ZnO layer was directly grown on *a*-plane Al_2O_3 substrate by using activated NO plasma as oxygen source and acceptor dopant.

6N-purity Zn, 5N-purity NO, and O_2 were used to grow the LED structure. For the *p*-type layer, NO was used as O source and N dopant simultaneously. Many experiments have indicated that not all N-dopants in ZnO can be activated into *p*-type carriers. To avoid double-donor doping of $N_{2(O)}$,[11] N_2 molecule content in the dopant should be decreased to as low as possible. In this work, an optical spectral unit was employed to monitor *in situ* the plasma emission from the NO species. Figure 1 shows typical emission spectrum of the NO plasma activated by a radio frequency atomic source. The emission lines at 746 nm, 777 nm, and those in the ultraviolet region, which originate from N atoms, O atoms, and N_2 molecules, respectively, were used to estimate the contents of the plasma species. The details of the growth processes for the *p*-type ZnO layers were reported elsewhere.[7] Hall-effect measurements showed that N-doped ZnO films are *p*-type, with hole concentrations of about 1.3×10^{17} cm^{-3}, and a mobility of 1.5 cm^2 V^{-1} s^{-1} at 200 K, while with increase of temperature, *p*-type conduction becomes unstable gradually. The *n*-type ZnO layer was grown by using Zn and O_2 as precursors and controlling the parameters without donor doping. The electron concentration and mobility of the *n*-type ZnO layers are 7×10^{18} cm^{-3} and 40 cm^2 V^{-1} s^{-1}, respectively.
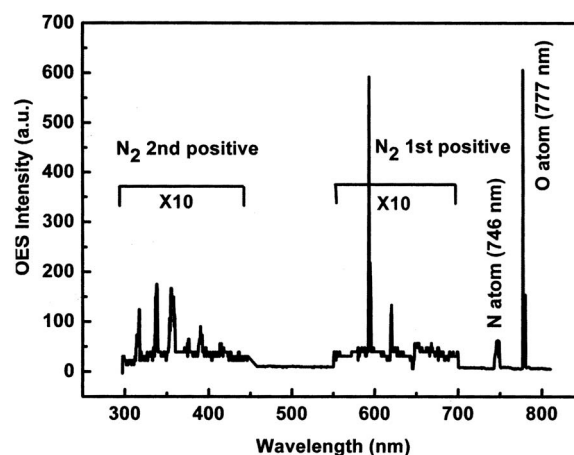

FIG. 1. Typical emission spectrum of NO plasma. The emissions at 746 (N atoms), 777 (O atoms), and ultraviolet region (N_2 molecules) are used to estimate the species contents of the plasma.

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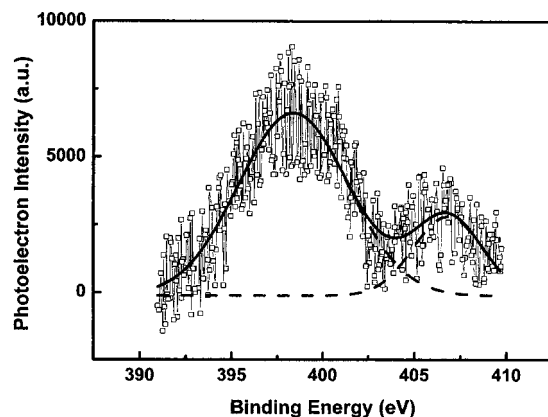
FIG. 2. A typical x-ray photoelectron spectrum obtained from the N-doped *p*-type ZnO film. The peak at 398.4 eV corresponds to the N 1*s* binding energy clearly indicated that N was incorporated in the ZnO film and acted as acceptor.

To identify the composition and chemical state of the doped nitrogen in the *p*-type ZnO layers, x-ray photoelectron spectroscopy measurement was conducted, as shown in Fig. 2. The Two peaks located at 406.8 and 398.4 eV, which correspond to the N 1*s* core level, clearly indicated that nitrogen was incorporated into the ZnO layers. The peak at 398.4 eV, which is a typical signal of N—Zn bond,[12] dominated the whole spectrum. This result confirmed the nitrogen substitution at the oxygen site (N_O) of ZnO, acting as acceptor. The peak appeared at higher binding energy 406.8 eV is due to the N 1*s* core electron of nitrite NO;[13] the contribution of this nitride dopant to conducting carriers, however, is still not clear.

The current-voltage (*I-V*) characteristics of the ZnO LED measured at temperature of $11-300$ K were shown in Fig. 3(a). The upper left inset shows the schematic structure of the ZnO *p-n* junction LED. A 200 nm thick *p*-type ZnO layer was grown directly on the *a*-plane Al_2O_3, which was capped by a 200-nm-thick *n*-type layer. Ni/Au and In electrodes were used to form ohmic contacts to *p*-type and *n*-type layers, respectively. At low temperature, the ZnO LED shows a good rectification characteristic with low leakage current. With increasing temperature, the leakage current increases and the rectification characteristic becomes inferior
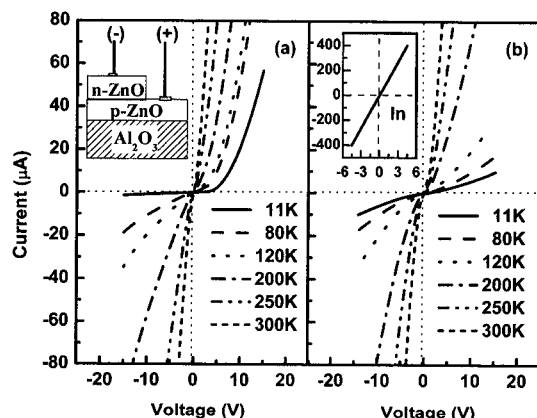

FIG. 3. (a) *I-V* characteristics of the ZnO LED at temperatures of $11-300$ K. The inset at top left corner is the schematic structure of the ZnO *p-n* junction LED. (b) The *I-V* characteristics of the Ni/Au−*p*-ZnO contact measured at temperatures from 11 to 300 K. The inset at the top left shows ohmic contact characteristics of the In−*n*-ZnO contact at room temperature.
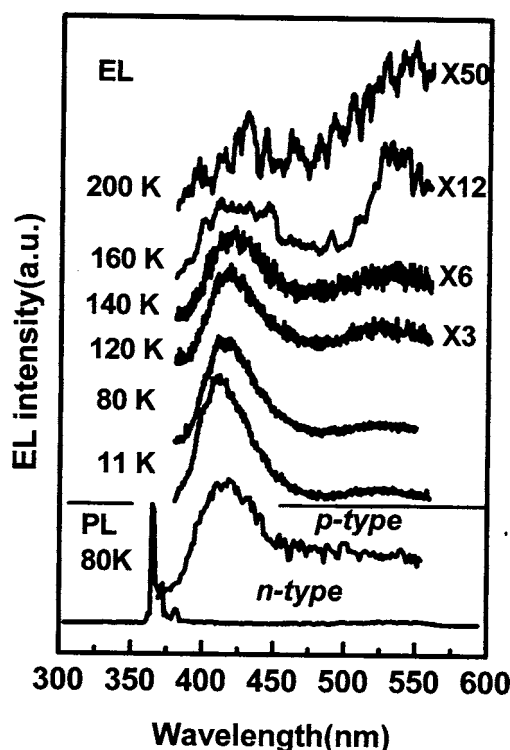

FIG. 4. EL spectra of the ZnO LED measured at temperatures of 11 to 200 K. The injection current was 130 μA. The lower panel of the figure shows the PL spectra of the *n*-type and *p*-type ZnO films grown on *a*-plane Al_2O_3 substrates, respectively, which were excited by the 325 nm line of a He–Cd laser at 80 K.

gradually. At room temperature, the reverse current is comparable with the forward one, and the LED does not show the rectification characteristics.

To analyze the influence of Ni/Au contact for *p*-type ZnO on *I-V* characteristics of the *p-n* homojunction, we verified the ohmic behavior between the Ni/Au electrode and the *p*-type ZnO layer. Figure 3(b) shows the *I-V* characteristics of the Ni/Au−*p*-ZnO contact as a function of temperature from 11 to 300 K. At low temperature ($11-120$ K), the linear *I-V* curve is a good indicator of ohmic contact between the electrode and the *p*-type layer, obviously different from the *I-V* curve of the *p-n* junction showed in Fig. 3(a). Within increasing temperature up to ~ 300 °C, the back-to-back Schottky behavior becomes more obvious, having a turn-on voltage of 1 V and a high leakage current. The results implied that the character of the Ni/Au−*p*-ZnO contact has gradually changed from ohmic to Schottky in the high-temperature region. As a comparison, the top left inset in Fig. 3(b) depicts the *I-V* characteristic of the In−*n*-ZnO contact at room temperature. The linear *I-V* line shape confirms the ohmic contact between the In electrode and *n*-ZnO layer. The *I-V* curves at higher temperatures showed that contact resistances between the metal electrodes and semiconductor layers increased significantly with temperature. This means that the conduction property of N-doped ZnO probably happens to change with increasing temperature.

The EL spectra at $11-200$ K are shown in Fig. 4, where the injection current is fixed at 130 μA. There exist two emission bands in the spectra: one is in the blue-violet region and the other is in the green region. Upon increasing temperature from 11 to 200 K, the blue-violet band shifts from 410 to 430 nm,   and   the   green   band   shifts   from
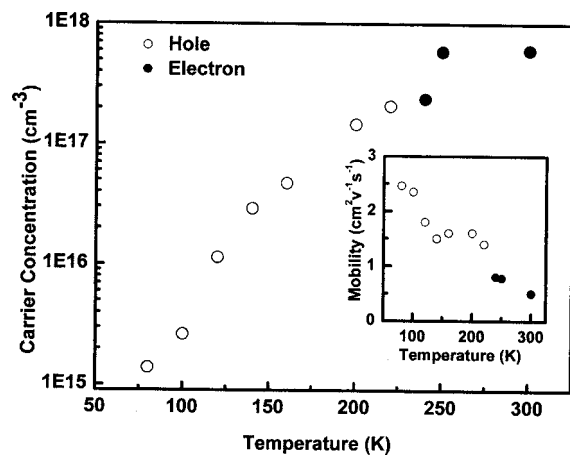
FIG. 5. Temperature dependence of the carrier concentration on the semilogarithmic scale. Inset shows mobility of N-doped ZnO film at different temperature.

520 to 540 nm. As seen, the EL decreased its emission intensity significantly with increase of temperature, and quenches at room temperature. This changing in intensity should be relative to the deterioration of *I-V* characteristics. To investigate the origin of the EL band, the photoluminescence (PL) spectra of the *p*-type and *n*-type ZnO films grown on sapphire substrates were measured, which were excited by 325 nm He–Cd laser at 80 K. As seen in Fig. 4, the EL spectrum at 80 K is similar with the PL spectrum of *p*-type ZnO at 80 K. For the *p-n* junction, because of low hole density and mobility of the *p*-type ZnO layer, the combination of carriers was dominated by the injection of electrons from the *n*-type layer to the *p*-type one. The PL band of the *p*-type layer appears at violet region from 400 to 460 nm, which can be attributed to donor-acceptor pair emission.[14] Therefore, as reported in Ref. 10, the EL emission should originate from the combination of donor-acceptor pairs in the *p*-type layer.

The electric characteristics of the *p*-type layer at different temperatures were measured to understand the *I-V* temperature dependence. Carrier concentrations as a function of temperature are plotted on a semilogarithmic scale in Fig. 5. It can be seen that the nitrogen doping lead to a stable *p*-type conduction at temperatures below 200 K, as measured by multiple measurement. The hole density increased from 4.3×10^{14} at 80 K to 1.3×10^{17} cm^{-3} at 200 K, while the hole mobility decreased from 2.4 to 1.5 cm^2 V^{-1} s^{-1} (see the inset of Fig. 5). At temperatures above 200 K, however, the *p*-type carriers were somehow compensated and the *p*-type conducting became unstable. This compensation became more and more significant with increase of temperature, and the probability of *n*-type measured by Hall effect was increased. At room temperature, a transition from *p*-type conducting to *n*-type conducting was observed in the nitrogen-doped ZnO layer. The mechanism of the *p*-type conducting degradation is not clear yet. Based on the criteria for *p*-type conducting in Hall measurement $p\mu_p^2 > n\mu_n^2$, two reasons for the degradation of the *p*-type conductivity in the high-temperature region can be considered as follows: (1) thermal ionization of some donor impurities in the *p*-type ZnO layer and (2) de-

crease of hole mobility. When hole mobility $\mu_p \leqslant 1$, Hall measurement is possible to show *n*-type, even if the sample is *p*-type in nature according to Look's explanation.[15] The degradations of *I-V* and EL at high temperature showed in Figs. 3 and 4 implied that the degradation of the *p*-type conduction is the main reason for the thermal quenching of the EL. With increasing temperature, the unstable *p*-type conducting lead directly to the large current leakage in the *I-V* curves showed in Fig. 3(a).

In conclusion, we fabricated a ZnO LED on Al$_2$O$_3$ substrate, where the *p*-type layer was obtained by using activated NO gas as O source and acceptor dopant. The ZnO LED showed typical rectification characteristics, and the threshold voltage for EL emission was as low as 4.0 V at 200 K. EL emission in the blue-violet region resulted from the radiative recombination transition of the donor-acceptor pair in the *p*-type layer of the LED. The deteriorations of the *I-V* and EL characteristics in the temperature region were attributed to the degradation of the *p*-type conducting of the nitrogen-doped ZnO layer.

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