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P- Type Conducting ZnSe and ZnSSe by N_2-Gas Doping during Molecular Beam Epitaxy

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Highly conductive *p*-ZnSe and ZnSSe can be grown by N_2-gas doping without any activation process during MBE growth. LEDs and LDs were fabricated using the N_2-gas doping method. The driving voltage of the LED was 3.8 V at the forward current of 20 mA. The threshold current density of the LD was about 1.4 kA/cm^2 at 77 K by pulsed operation. The oscillation of the ZnSe based LD fabricated without N-radical doping technique was achieved for the first time.

1. Introduction

Recently, ZnSe-based photo devices have been developed to a remarkable level, demonstrating continuous wave operation of a blue-green laser diode (LD) at room temperature [1, 2]. All the ZnSe-based LDs reported were fabricated using a N-radical doping technique. The N-radical doping technique is a novel N doping method using an active N generated by rf or ECR discharge[3, 4]. The active N has a high sticking coefficient to ZnSe in MBE growth. Before utilizing the N-radical doping technique, there were some reports on attempts to fabricate N-doped ZnSe by N^+ ions, N_2 gas and NH_3 gas. Park, *et al.* reported that shallow acceptors were formed by N_2 and NH_3 gas doping, but no *p*-type conduction was reported[5]. These results were accredited to the fact that the sticking coefficients of N_2 and NH_3 molecules are so low as to produce enough N concentration in ZnSe to exhibit *p*-type conduction. Mitsuyu, *et al.* reported N-doped ZnSe by MBE with an ion doping technique for increasing the sticking coefficient[6]. Although highly N-doped ZnSe were obtained by irradiating a partially ionized beam of NH_3 during MBE growth, the resistivity of the ion doped films was very high ($\rho > 10^4\ \Omega$ cm). Therefore, in order to obtain *p*-type conducting ZnSe by N-doping, it has been believed that the N-radical doping technique during MBE growth is the only practical way to fabricate it.

However, through detailed investigation, we have found that *p*-type conducting ZnSe and ZnSSe can be grown with good reproducibility by simple N_2-gas doping during MBE growth without any activation method[7]. This result is very interesting with regard to the development of *p*-type doping in ZnSe. In this paper, we report on the properties of N_2-gas doped ZnSe and ZnSSe, and compare them with films doped by other N doping techniques. Moreover, we also report on ZnSe-based light emitting diodes (LEDs) and LDs, in which all of the *p*-type layers were fabricated by N_2-gas doping.

2. Experimental procedures

N_2-gas doped films were grown by MBE. Elemental Zn (99.99999% purity), Se (99.9999% purity), and ZnS compound (99.999% purity) were used as source materials. $CdCl_2$ was used as the Cl source for *n*-type doping. N_2 (99.9999% purity) dopant gas supplied from an external gas cylinder was introduced using an Oxford Applied Research model MPD-20 radical beam source without rf power operation, which was used as a mere N_2-gas cell. N_2 beam pressure was regulated by a needle valve. *P*-type Zn-doped and *n*-type Si-doped GaAs (100) were used as substrates. Before being inserted into the MBE system, the substrate was degreased and chemically etched in a solution of H_2SO_4-H_2O_2-H_2O (5:1:1) for 1 minute at 60°C. Prior to growth, the substrate was heated at 640°C for 3 min. (for *p*-GaAs) or at 610°C for 10 min. (for *n*-GaAs) in an ultrahigh vacuum to remove the native oxide, and then heated at a growth temperature. During growth, the Zn and Se beams were kept at 1.2×10^{-7} and 1.8×10^{-7} Torr, respectively. When the ZnSSe film was grown, the Zn, Se and ZnS beams were kept at 1.2×10^{-7}, 1.8×10^{-7} and 4×10^{-8} Torr, respectively. Under these conditions, ZnS_xSe_{1-x} alloy with composition X of 0.06 was grown. The grown films were characterized by photoluminescence (PL) and capacitance-voltage (*C-V*) measurement techniques. Net acceptor concentration (N_A-N_D) was measured by the capacitance-voltage method. All *C-V* measurements were performed using concentric circular Ti/Au electrodes and a measurement frequency of 100 kHz.

3. Photoluminescence properties of N-doped ZnSe

Figure 1 shows the PL spectra of the N-doped ZnSe films doped by the N_2-gas (a) and N-radical (b) doping methods. The N_2-gas doped film (a) was grown under N_2 pressure of 1×10^{-4} Torr without any activation method, such as discharge and cracking. The N-radical doped film (b) was a lightly doped sample grown under an N-radical beam pressure of 5×10^{-6} Torr and rf power of 100W. The N_A-N_D of the N_2-gas and N-radical doped films was 2×10^{17} cm^{-3}. Both the spectra were dominated by strong I_1^N, free excitonic and donor to acceptor pair (DAP) emissions. The variety and energy of the luminescent peaks of the N_2-gas doped sample are similar to those of the spectra from lightly N-doped ZnSe. The similarity of these spectra indicates that N atoms are incorporated as shallow acceptors in ZnSe by N_2-gas doping during MBE and that they produce *p*-type conduction.

We have also tried NH_3 (99.99% purity) doping for N-doped ZnSe. We found that N-doped ZnSe is grown by doping with cracked NH_3 when it is cracked above 800 °C. Figure 2 shows the PL spectra of cracked NH_3 doped ZnSe. The film was grown at 320 °C with 2×10^{-8} Torr of cracked NH_3 beam heated at 950 °C. Although the cracked NH_3

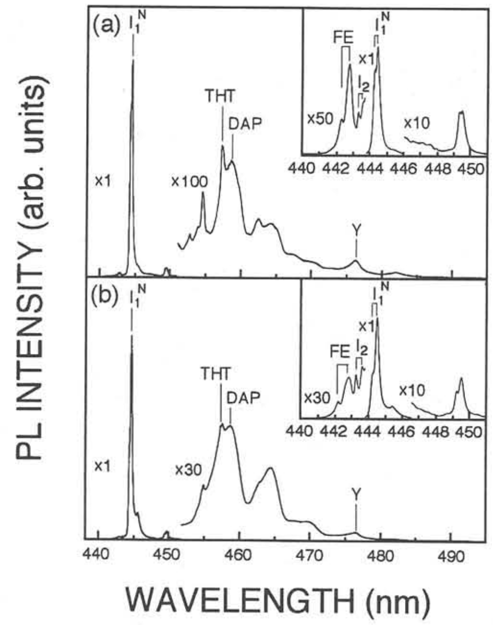

Fig. 1. 16K PL spectra of N-doped ZnSe grown by N_2-gas doping (a) and N-radical doping (b), excited by He-Cd laser 325 nm emission. Free excitonic, donor-bound excitonic, N-acceptor bound excitonic, two-hole or free to acceptor, donor acceptor pair, and Y emissions are indicated as FE, I_2, I_1^N, THT, DAP, and Y, respectively.

beam pressure was about 2-4 digits lower than the N_2 and N-radical pressure discussed above, strong DAP and weak excitonic emissions were observed in the spectra. The DAP emission was as intense as that of heavily N-radical doped samples. This result indicates that the cracked NH_3 sticks ZnSe efficiently and forms dense N-acceptors in the film. However, no *p*-type conductivity was observed in the cracked NH_3 doped ZnSe. The reason for this is not yet clear. We speculate that N-acceptors were compensated by a difficulty peculiar to NH_3 and residual impurities, because the I_2 emission of cracked NH_3 doped ZnSe was stronger than those of N_2-gas and N-radical doped ZnSe.

From the comparison between the results of N_2-gas, N-radical and cracked NH_3 doping, N_2 is considered to be adequate as a N source for N-doped ZnSe, but *p*-type ZnSe

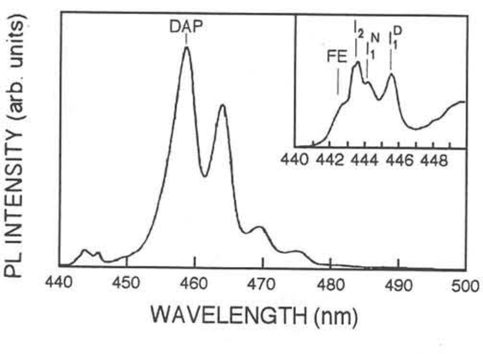

Fig. 2. 16K PL spectra of cracked NH_3-doped ZnSe, excited by He-Cd laser 325 nm emission. Free excitonic, donor-bound excitonic, N-acceptor bound excitonic, and donor acceptor pair emissions are indicated as FE, I_2, I_1^N, and DAP, respectively.

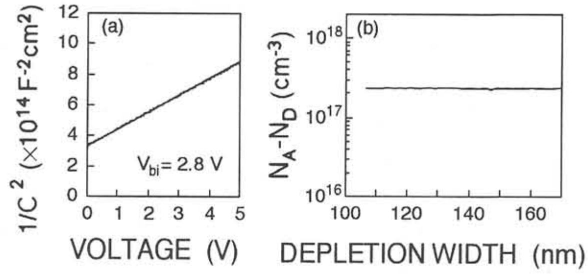

Fig. 3. $1/C^2$ vs. V (a) and N_A-N_D vs. depletion width (b) profiles of N_2-gas doped $ZnS_{0.06}Se_{0.94}$ which was grown under N_2 pressure of 1×10^{-4} Torr.

with NH_3 doping seems to be difficult to fabricate.

4. Electronic properties of N_2-doped ZnSe and ZnSSe films

Figures 3 (a) and (b) show the typical $1/C^2$ vs. V and N_A-N_D vs. depletion width profiles of the N_2-gas doped film, respectively. Figure 4 shows the relationship between the N_2 pressure and N_A-N_D of N_2-gas doped ZnSe and $ZnS_{0.06}Se_{0.94}$ films. When the N_2 pressure was increased from 3.2×10^{-5} to 1×10^{-4} Torr, the N_A-N_D of the N_2-gas doped ZnSe and ZnSSe gained from 3×10^{15} to 2×10^{17} cm^{-3} and from 1×10^{16} to 2.5×10^{17} cm^{-3}, respectively. These results indicate that their N_A-N_D are controlled by the regulation of N_2 pressure and that the doping efficiency of N_2-molecules to ZnSSe is as good as that to ZnSe. This result differs from the result reported by Park, *et al.*[5], in which no *p*-type conductivity was observed while N_2-gas doping was carried out under almost the same ion gauge reading of N_2 pressures as our present work. We speculate that the N_2-molecule impinging rate on the substrate of our experiment might not be the same as that by Park. The indication of N_2 pressure measured by the ion gauge is the sum of the incident beam and the background pressure. Though the ion gauges indicate the same pressure, incident effective N_2-beam pressures can possibly differ provided that the pumping speeds of the MBE system are not the same. The difficulty in fabricating *p*-ZnSe by N_2-gas doping reported previously results simply from the low sticking coefficient of the N_2 molecule. A large

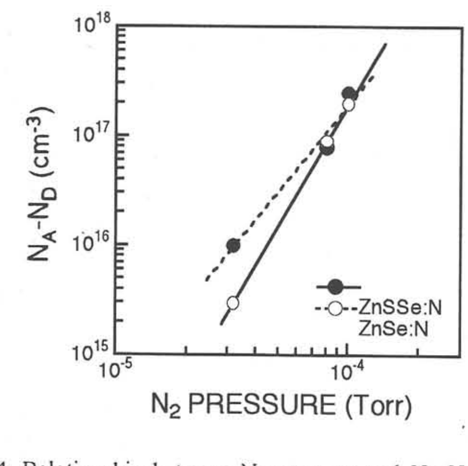

Fig. 4. Relationship between N_2 pressure and N_A-N_D of N_2-gas doped ZnSe and $ZnS_{0.06}Se_{0.94}$ films.

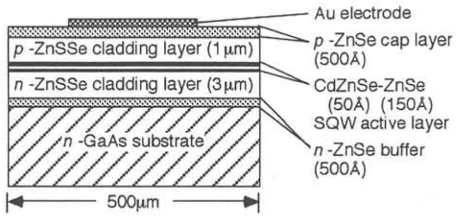

Fig. 5. The schematic structure of the LED.

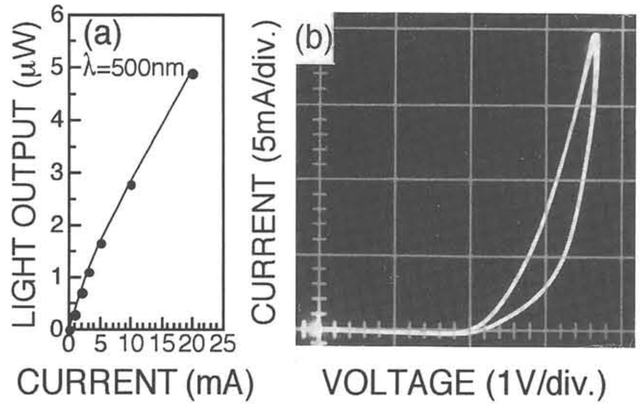

Fig. 6. L-I and V-I characteristics of the LED.

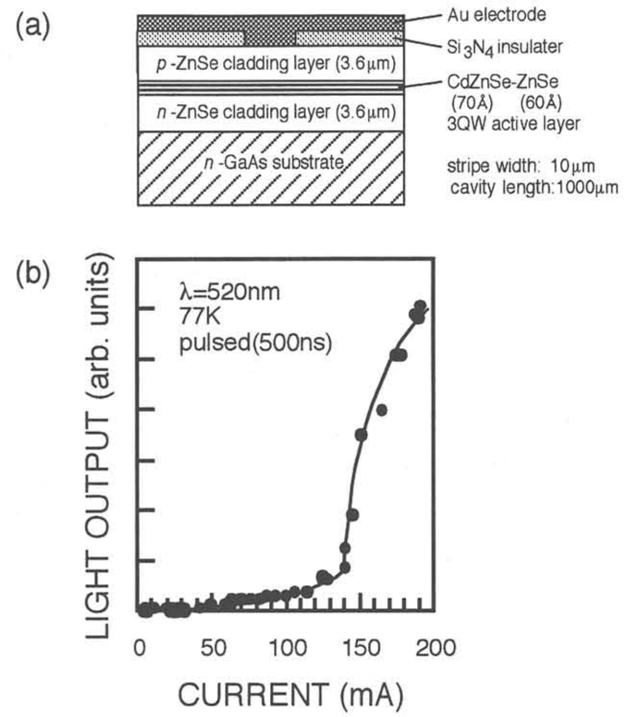

Fig. 7. The schematic structure (a) and *L-I* characteristics (b) of the LD.

amount of N_2 beam irradiation during the MBE process enables a *p*-type conducting ZnSe.

5. Photo device applicability of N_2-gas doping method

In order to examine the photo device applicability of the N_2-gas doping method, we fabricated and tested LEDs and LDs. No *p*-type layers were fabricated for them using the N-radical doping method. Figure 5 shows the schematic structure of the LED. The *p*-ZnSSe cladding and *p*-ZnSe cap layers were fabricated by N_2-gas doping. An Au electrode was deposited directly onto the *p*-ZnSe cap layer. Figures 6 (a) and (b) show the light-current (*L-I*) and the voltage-current (*V-I*) characteristics of the LED, respectively. Light output power of 4.9 μW was obtained at the forward current of 20 mA when the diode was driven at the forward voltage of 3.8 V. The driving voltage of the diode fabricated using the N_2-gas doping method is lower than that fabricated by the N-radical technique. Figures 7 (a) and (b) show the schematic structure and *L-I* characteristics of the LD. The threshold current density was about 1.4 kA/cm^2 when it was driven at 77 K by pulsed operation. The oscillation of the ZnSe based LD fabricated without the N-radical doping technique was achieved for the first time. The operating voltage around the threshold was about 15 V. This driving voltage was also lower than that of a similar structural LD with N-radical doping fabricated in our laboratory.

6. Summary

We found that highly conductive *p*-ZnSe can be grown by N_2-gas doping without any activation process during MBE growth. Using the N_2-gas doping method, we achieved the oscillation of the ZnSe based LD to be fabricated without the N-radical doping technique for the first time. The threshold current density of it was about 1.4 kA/cm^2 when it was driven at 77 K by pulsed operation. We also found that the driving voltage of LEDs and LDs fabricated by the N_2-gas doping method is lower than that of similar structural devices fabricated with the N-radical doping technique.

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