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Red emission from ZnO-based double heterojunction diode

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1. Introduction

Wurtzite-type ZnO has some typical features such as a direct band gap energy (Eg) of 3.28 eV and a large excitonic binding energy of 60 meV at room temperature. We have successfully demonstrated ZnO-based semiconductors systems utilizing remote plasma enhanced metal organic chemical vapor deposition (RPE-MOCVD), exhibiting a band gap energy from 1.8 eV[1-2] to 3.7 eV[3]. In addition, we have recently achieved full-color electroluminescence (EL) emissions from ZnO-based hetetojunctions on *p*-4H-SiC substrates[4]. However, their full widths at half maximum (FWHMs) were relatively large of around 315 meV.

In this paper, we focus on an improvement of $Zn_{1-x}Cd_xO$ film quality with the red emission by utilizing thermal annealing process and the performance of red emission with a narrower FWHM from ZnO-based double heterojunction (DH) diode.

2. Experimental

ZnO-based films have been grown by remote plasma enhanced metal organic chemical vapor deposition (RPE-MOCVD) using DEZn, DMCd, $EtCp_2Mg$ and oxygen radical generated by a radio frequency (RF) of 13.56 MHz as material sources. A-plane sapphire substrates and *p*-4H-SiC substrates (Eg=3.26eV) for electroluminescence measurements were used. Growth conditions for red emission $Zn_{1-x}Cd_xO$ films are shown in table. 1. The DH junction diode basically consists of *n*-ZnO cap layer, *n*-$Mg_{0.12}Zn_{0.88}O$ cladding layer and *n*-$Zn_{1-x}Cd_xO$ emission layer and $Mg_{0.12}Zn_{0.88}O$:N barrier layer on *p*-4H-SiC substrates. Indium and aluminum were used as the electrodes.

We have characterized the band gap energies using optical transmission measurements and photoluminescence analysis. The contents of the films were analyzed by atomic absorption spectroscopy.

Table 1. Growth conditions of $Zn_{1-x}Cd_xO$ in case of red region.

DMCd/(DEZn+DMCd)	0.5
Growth temperature	350 ～ 500 ºC
RF power	20 W
Growth pressure	0.01 Torr
Substrate	a-plane (11-20) sapphire

3. Experimental results and discussion

Fig. 1 summarizes the achieved band gap energy corresponding to the alloy content of wurtzite-type ZnO-based systems. This relationship indicates that ZnO-based semiconductors are potential candidates for optical devices with the whole wavelength range between the visible and UV. Fig. 2 shows the growth temperature dependencies of the optical and structural qualities of $Zn_{1-x}Cd_xO$ films with around red emissions of 1.9 eV. The experimental data of ZnO films are also included as a reference. It is found that the photoluminescence PL emission energy does not remarkably change for the substrate temperatures between 350 to 500 ºC. However, the FWHMs of PL and X-ray diffraction of the c-axis orientation are drastically increased with higher substrate temperature. Here, we have chosen the proper substrate temperature as 400 ºC and tried to improve the optical quality and the crystal structure of the $Zn_{1-x}Cd_xO$ films by adopting a thermal annealing process. We have particularly focused on the atmosphere effect in the annealing conditions. The annealing temperature is chosen as 500 ºC. In Fig. 3(a), PL spectra from $Zn_{1-x}Cd_xO$ films are shown under the vacuum, N_2, and air conditions including the as-grown data. Fig. 3(b) summarizes their optical properties versus the various conditions, indicating that the annealing in vacuum provides an improvement in terms of PL intensity and the FWHM. In this way, we have achieved a FWHM of 126 meV for the $Zn_{0.5}Cd_{0.5}O$ film annealed under vacuum condition. The annealed data is comparable to the FWHM (126 meV) of the ZnO film as shown as an inset in Fig. 2. In addition, the Stokes shift for the annealed sample is drastically decreased to 30 meV, compared with as-grown one. These results suggest that the thermal annealing in vacuum improves a microscopic inhomogeneity in the ternary alloy films.

We have fabricated a ZnO-based double heterojunction films structure by particularly introducing the annealing technique for the $Zn_{1-x}Cd_xO$ film. The vertical structure is based on the previous one[4] and includes the nitrogen-doped $Mg_{0.12}Zn_{0.88}O$ film for *p*-type conduction on *p*-4H-SiC substrate. Fig. 4 shows EL spectrum from ZnO-based double heterojunction diode. While it seems there are two emission peaks at around 1.9 eV and 2.8 eV, the lower energy peak at 1.9 eV (red) is coming from the $Zn_{1-x}Cd_xO$

film. The FWHM is estimated as 213 meV, which is much smaller than that (388 meV) of the as-grown DH reference sample without an annealing process. It seems that the broader higher energy peak at around 2.8 eV is coming from the substrate-side interface of the *p*-4H-SiC due to the electron injection, which suggests the *n*-type conduction of the $Mg_{0.12}Zn_{0.88}O$:N film on the *p*-4H-SiC substrate. In comparison with p-ZnO:N[5], the reproducibility of *p*-$Mg_yZn_{1-y}O$:N is considered to be a problem. However, the improvement approach is in progress and a suppression of the higher energy emission will be expected.

4. Conclusion

We have demonstrated wurtzite-type ZnO-based ternary alloy systems by RPE-MOCVD, showing the controlled band gap energy from 1.8 eV up to 3.7 eV. We have succeeded to improve the crystal quality of $Zn_{1-x}Cd_xO$ system by introducing the annealing process and achieved the red EL emission with the improved FWHM of 155 meV from the ZnO-based double heterojunction diode.

References

1) J. Ishihara, A. Nakamura, S. Shigemori, T. Aoki, and J. Temmyo, Appl. Phys. Lett. **89** (2006) 091914.
2) T. Ohashi, K. Yamamoto, A. Nakamura, T. Aoki, and J. Temmyo, Jpn. J. Appl. Phys. **46** (2007) 2516.
3) K. Yamamoto, K. Enomoto, A. Nakamura, T. Aoki, and J. Temmyo, J. Cryst. Growth. **298** (2007) 468.
4) A. Nakamura, T. Ohashi, K. Yamamoto, J. Ishihara, T. Aoki, and J. Temmyo, Appl. Phys. Lett. **90** (2007) 0903512.
5) S. Gangil, A. Nakamura, Y. Ichikawa, K. Yamamoto, J. Ishihara, T. Aoki, and J. Temmyo, J. Cryst. Growth. **298** (2007) 486.

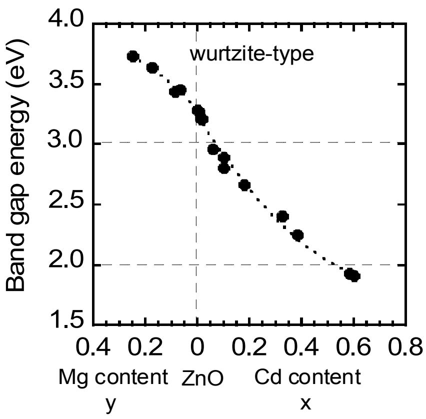

Fig. 1 Band gap energy of wurtzite-type ZnO-based alloy films versus their contents.

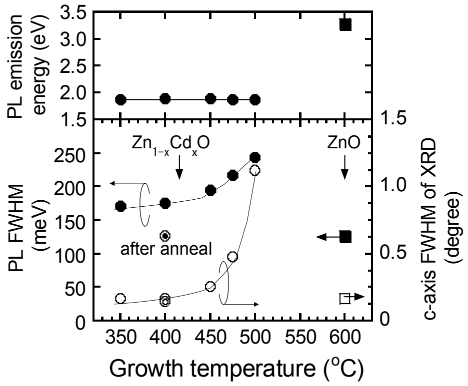

Fig. 2 Growth temperature dependencies of characteristics of $Zn_{1-x}Cd_xO$ alloy films. The results on ZnO film are also included.

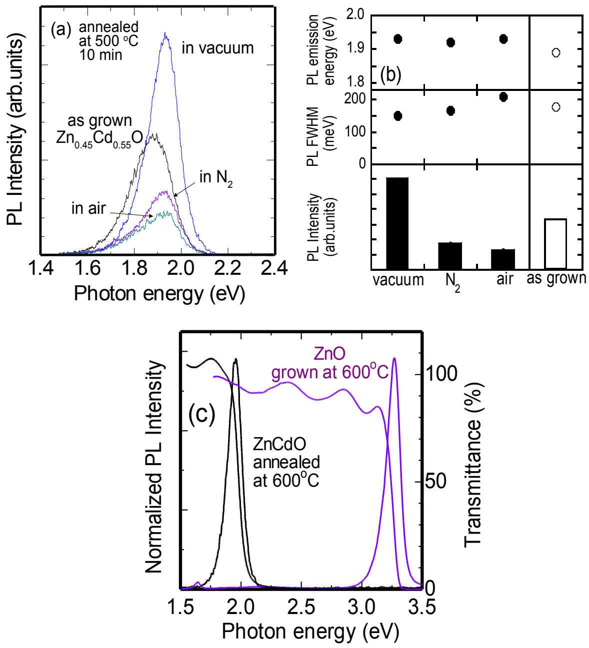

Fig. 3 (a) PL spectra from $Zn_{1-x}Cd_xO$ films annealed in various atmosphere.
(b) PL Intensity and PL FWHM versus annealing atmosphere.
(c) Optical property of $Zn_{1-x}Cd_xO$ films annealed at 600 °C and as-grown ZnO at 600 °C.
Their transmittance spectra are also included.

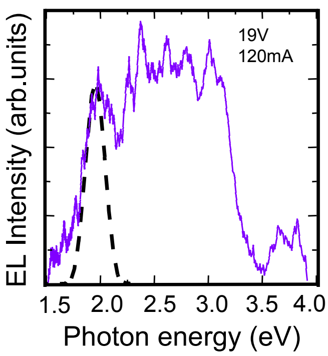

Fig. 4 EL spectrum from ZnO-based DH junction with the annealed $Zn_{1-x}Cd_xO$ emission layer.