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Stimulated Emission from ZnSe-Based Laser Diode Structure Grown by Photoassisted MOVPE with Annealing Technique

K. Ogata, N. Nishiyama, D.Kawaguchi, G. Peng, Sz. Fujita and Sg. Fujita

Department of Electronic Science and Engineering, Kyoto University, Kyoto 606-01, Japan
Phone: +81-75-753-5357, Fax: +81-75-753-5898, E-mail: k-ogata@kuee.kyoto-u.ac.jp

1. Introduction

Increasing of the lifetime of blue-green laser diodes (LDs) grown by molecular beam epitaxy (MBE) more than 100hours [1] is opening the key for the practical device application of II-VI semiconductors. On the other hand, by metal organic vapor phase epitaxy (MOVPE), which is more superior in mass production and compostion control of alloy semiconductors, the difficulty of p-type conductivity control has been obstructing the fabrication of optical devices such as LED or LD. Recently, a Sony group reported the first pulsed lasing operation at 77K from MOVPE-grown ZnCdSe/ZnMgSSe LD structure. However the net acceptor concentration ($N_A - N_D$) achieved for p-type ZnSe:N was still about $1\times10^{16}cm^{-3}$ [2], whereas the nitrogen concentration was $1\times10^{18}cm^{-3}$, showing heavy passivation of acceptors by hydrogen.

Until now, we have reported that thermal annealing technique was effective to reduce the hydrogen passivation and p-type ZnSe:N exhibited $N_A - N_D$ as high as $5\times10^{17}cm^{-3}$ [3]. It is, therefore, widely accepted as one of the most promising methods for obtaining highly conductive p-type ZnSe:N and for possessing high potential for device application. However, in fabrication of optical devices, effects of annealing process not only on p-type layers but also on n-type layers and active layers must be considered. In this paper, we discuss the optimum growth and annealing conditions for the device fabrication, and show stimulated emission from ZnCdSe/ZnSe/ZnSSe single quantum well (SQW) separate confiment heterostructure (SCH).

2. Effects of annealing n-type ZnSSe layers and ZnCdSe active layers

Epitaxial growth of ZnSSe was carried out on (100) oriented GaAs substrates with source precursors of diethylzinc (DEZn), dimethylselenide (DMSe) and diisopropylsulfide (Di-PS) by photoassisted MOVPE. For p-type ZnSSe:N layers nitrogen doping was made with tertiarybutylamine (t-BuNH$_2$) at 350°C, and for n-type ZnSSe:I iodine with normalbutyliodine (n-BuI) at 350~450°C.

In order to obtain p-ZnSSe:N where $N_A - N_D$ is higher than $10^{17}cm^{-3}$, thermal annealing higher than 450°C has been needed. On the other hand, by annealing process at 450°C, n-ZnSSe:I layers grown at 350°C get high resisitivity due to heavy degradation. The different degree of degradation of p-type and n-type layers seems to be due to the fact that in ZnSSe:N layers there exists the phenomena like solution hardening [4]. Therefore for fabrication of pn-junction by the annealing process, it is very important to minimize the degradation of n-ZnSSe:I. In order for less degradation of n-type layers, attempts were made to grow ZnSSe:I at higher growth temparature. Carrier concentration of ZnSSe:I grown at 450°C did not reach the order of $10^{16}cm^{-3}$, which was attributed to the decrease in the sticking coefficient of iodine at high temperature [5]. However, for the growth at 400°C it could be the middle of $10^{17}cm^{-3}$ and did not show heavy degradation after the annealing at 450°C. This means that the growth at 400°C of n-ZnSSe:I allows fabrication of pn-junction diodes.

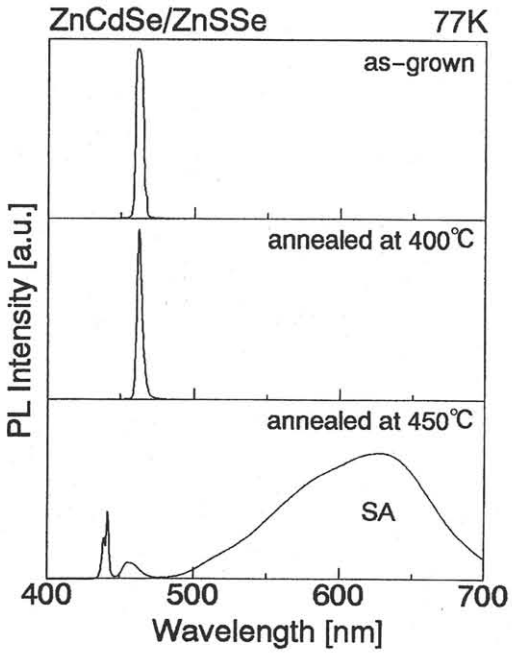

Fig.1 PL spectra at 77K from ZnCdSe/ZnSSe SQW structure subjected to annealing at different temperatures

For obtaining higher carrier concentration of n-ZnSSe:I, we need further underatanding of degrada-

tion mechanism due to annealing, using for example, positron annihilation method [6] or deep level transient spectroscopy (DLTS) [7].

Another problems toward LDs are related to ZnCdSe active layers. One of them is difficulty of precise control of Cd compostion under photoirradiation at low temperature [8], and an another is large strain in ZnCdSe. Therefore the growth was done using dimethylcadmium (DMCd) *without* photoassistance at 450°C, and the Cd content was kept as low as 10% for supression of strain-induced degradation during the annealing process. In Fig.1, we show the annealing temperature dependence of photoluminescence (PL) spectra at 77K from $Zn_{0.9}Cd_{0.1}Se$/ZnSSe SQW structure. In our experiments, ZnCdSe/ZnSSe SQW structure was stable by annealing at 400°C, but the structure interdiffused or relaxed at 450°C. Then, for the time being, we may say that the annealing temperature should be lower than 400°C in order to avoid degradation of the SQW structure. Taking into account of these problems at the present stage, we cannot choose the annealing conditions without sacrificing the maximum activation of acceptors.

3. Emission from LD structure

Based on the results mentioned above, we fabricated a ZnCdSe/ZnSe/ZnSSe *pn*-junction SQW-SCH structure on an n^+-GaAs substarate with annealing at 400°C. Thicknesses of *n*-ZnSSe, ZnSe, ZnCdSe, and *p*-ZnSSe:N are 1.1μm, 500Å, 50Å, and 1.4μm, respectively.

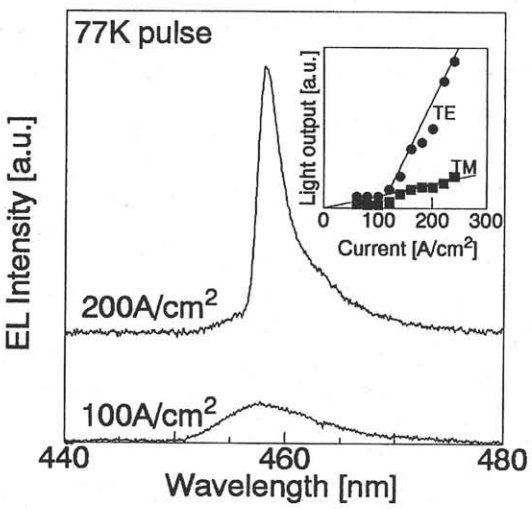

Fig.2 Polarization dependence of emission intensity from LD structure

For reduction of the current spreading, 50μm-wide mesa stripe structure was fabricated, and gold was evaporated on *p*-ZnSSe:N as the electrode. As shown in Fig.2, emission from $Zn_{0.9}Cd_{0.1}Se$ active layer by current injection was observed at 77K, and TE polarized emission from the cleaved surface was superlineary enhanced above 120A/cm^2 pulse injection, suggesting successful stimulated emission. However, in this annealing condition, the $N_A - N_D$ of *p*-type layer was limited to be lower than 10^{16}cm^{-3}. Therefore in order to increase the $N_A - N_D$ of *p*-ZnSSe:N in LD structures, efforts on the other annealing techniques such as rapid thermal annealing are under progress.

4. Conclusion

In order to utilize the annealing technique for device fabrication, effects on *n*-type ZnSSe:I and ZnCdSe active layers were investigated. To reduce the degradation of *n*-ZnSSe:I during annaling, the growth temperature was chosen to be 400°C. On the other hand, the effects on ZnCdSe active layers are serious. Sufficient activation of acceptors and supression of degradation of active layers are not consistent at the present stage. However, in order to show the present technological stage, we fabricated LD structures, where TE polarized emission was superlinerly enhanced above 120A/cm^2, suggesting stimulated emission. A novel annealing technique in the future will allow the maximum activation of acceptors and the minimum degradation simultaneously.

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