Extended Abstracts of the 1997 International Conference on Solid State Devices and Materials, Hamamatsu, 1997, pp. 202-203

Shallow-Deep Transition of Nitrgen Acceptor in Blue Semiconductor Laser Material ZnMgSSe

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1. Introduction

Detailed understanding the degradation mechanism of II-VI blue laser diodes (LDs) has become very important issue since the demonstration of room-temperature CW operation [1]. Recent study on the degradation mechanism of the II-VI blue LDs by Sony reseach Group has pointed out that micrscopic point defects play important role to enhance the generation and the propagation of macroscopic defects, leading to the short life time of LD devices [2]. We have made a systematic study on the point defects in II-VI blue laser materials, ZnSe, ZnSSe and ZnMgSSe and found that the radical nitrogen (acceptor) doping has induced high density electrically active centers (carrier compensation / nonradiative recombination centers) which strongly affects the device characteristics and life time [3-4].

This paper presents a unique and important behavior; shallow to deep level transition, of an effective-mass acceptor (N:nitrogen) in p type ZnMgSSe quaternary system grown by molecular beam epitaxy (MBE). This metastable center is also found to cause marked PPC (persistent photo-conduction) effect and which looks similar to the nature of the DX center in AlGaAs system [5]. Here we present direct evidences on the defect structure-transformation (shallow to deep level) of N acceptor and a new defect levlel transition model including a shallower acceptor-like center in p ZnMgSSe system.

2. Experiments

The sample used is N doped p type $Zn_{1-x}Mg_xS_ySe_{1-y}(0<x<0.18, 0.1<y<0.2)$ films with effective carrier density (N_a-N_d) of $0.5\text{-}1\times10^{17}cm^{-3}$ at room temperature, which is grown by a conventional MBE on the (100) GaAs substrates. Reversible change in the (N_a-N_d) and deep defect center (HM1 center) densities under light excitation (zero-electric field) at low-temperature are studied by 4-terminal Hall measurement, capacitance-voltage (C-V) curve, and by a deep level transient spectroscopy (DLTS, ICTS) techniques. A thermally-stimulated capacitance (TSCAP) experiemnt is also carried out to find the relation between the deep and shallow acceptor centers. In this study, marked structural instability of effective-mass acceptor ([A^0]: E_A=170-195 meV) does not exist in ZnSe(binary), ZnSSe(ternary) but is only detected for the p type ZnMgSSe quaternary system with x>0.05.

3. Results and Summary

The main results on the defect reaction obtained are sumarrized as follow:

(i) Light excitation under low temperature ($h\nu > E_g$, T<150K) is found to generate a deep hole trap center (HM1: E_v+550±140 meV) and this deep center has disappered again under the dark or strong electric field condition (shown in Fig.1)

(ii) This excitation has induced a new undefined shallower acceptor [A*] with activation energy E_{A*}= 90-105 meV. This energy is about half of that for the usual effective mass acceptor [A^0] of nitrgen. The reduction of the carrier (hole) density is completely recoverd again with increasing temerature to 300K [6] .

(iii) Distinct PPC effect is taken place under strong light illumination in150-220 K. ,where N_a-N_d has decreased and the deep HM1 center has been induced. Optical threshold energy for the PPC is determined as $E^0(h\nu_o)$= 1.65 eV (far below bandgag energy) and the photo-excited carrier relaxation vs. increasing temperaure is dominated in an exponential decay formulation with ΔE(decay) = 490 meV (shown in Fig.2).

These results clearly indicate the occurence of a large lattice-relaxation type shallow-deep transition between the effective mass acceptor [A^0] and deep HM1 center. A unique feature of the present defect reaction is that unexpected *shallower acceptor like center* [A*] has generated at low temperature just before the appearance of the deep center. So, we present one possible defect reaction model :

$$2A^*[0] \dashrightarrow AX[+] + A^0[-]. \quad \text{----- (1)}$$

Here the A* is produced at low temperature by light excitation, the (AX) is generated deep center(used instead of the deep HM1 center). The detailed defect relation mechanism including [A], [A*] and [Deep centers:AX] and its influence on the devices instability and device life-time are also discussed.

References

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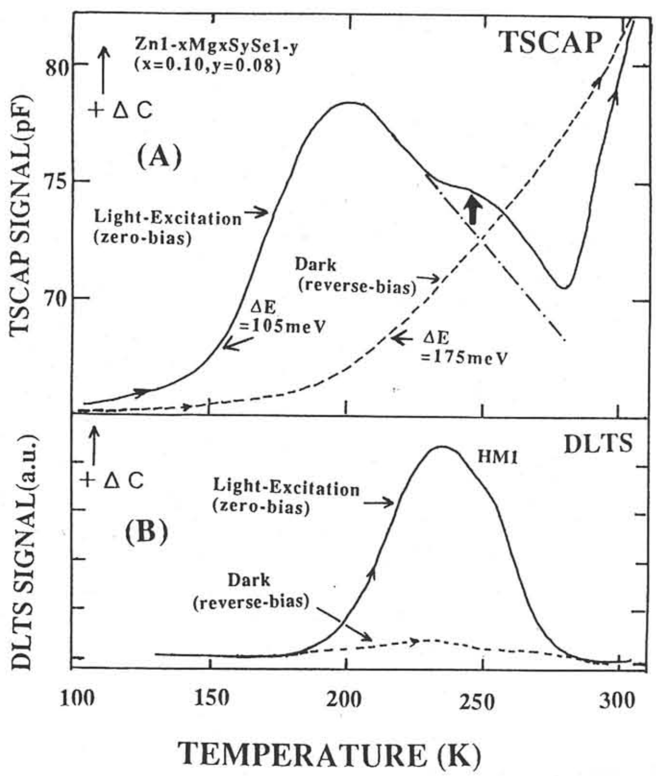

Fig.1: (A) TSCAP curves for two different initial conditions: (i)light excitation(5 min at 100K under zero-bias)and (ii)dark under 3V reverse-bias. (B) DLTS spectrum for dark and light excitation conditions at 100K. The HM1 center has generated under light excitation condition and this center disappeared again in dark(reverse bias) condition.

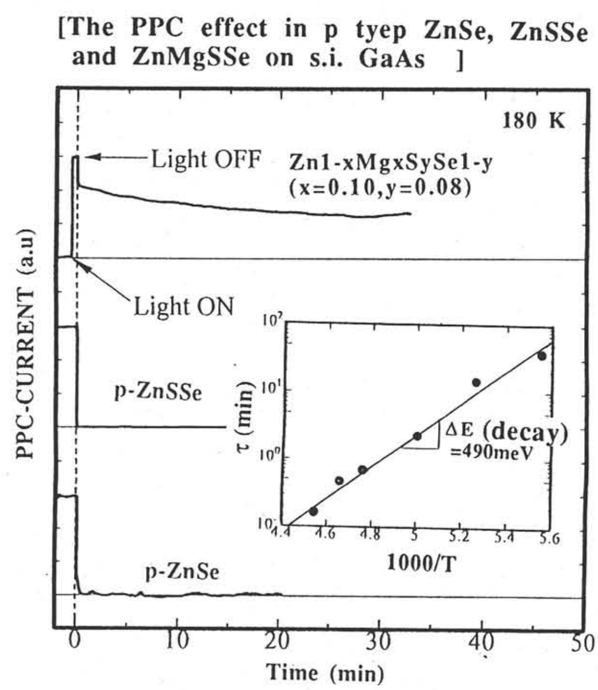

Fig.2: Light excitation effects on the residual photo-current(PPC). The marked PPC is observed only for p type ZnMgSSe grown on s.i. (100)GaAs. Inset shows Arrhenius plots for the photo-carrier decay time constant for the temperature.