Extended Abstracts of the 20th (1988 International) Conference on Solid State Devices and Materials, Tokyo, 1988, pp. 415-418

D-9-7

Blue Luminescence Efficiency of Chlorine Doped ZnSe Grown by MOCVD

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The photo- and cathode luminescence of a chlorine doped ZnSe layer, grown by MOCVD on a GaAs substrate, has been studied. The blue donor-to-band recombination dominated photoluminescence was observed at room temperature. The external quantum efficiency for this blue luminescence at 300 K was estimated to be 0.016% (internal quantum efficiency: 2.5%) at a low excitation density of 10^{21} e/h pairs cm^{-3} sec^{-1}. An internal quantum efficiency at a moderate excitation density for LED (10^{23} e/h pairs cm^{-3} sec^{-1}) as high as 25% (at $n=2\times10^{17}$ cm^{-3}) was deduced from the excitation density dependence of blue luminescence.

1. INTRODUCTION

ZnSe has a large potential for blue emitting diodes and lasers. Many investigations have been reported on the growth of ZnSe on GaAs substrates by MOCVD, MBE, and a few other epitaxial growth methods. Good qualities of photoluminescence spectra at 4.2 K and microscopic images have been reported on these epitaxial layers. Recently, blue luminescence dominated PL spectra at room temperature were reported in some papers[1,2] on VII group element doped ZnSe layers. These doping processes have good controllability of carrier concentrations. Applications of these layers to blue emitting devices are expected. The emission efficiency is an important parameter for designing light emitting devices. However, it has been reported only in an undoped epitaxial layer[3]. In the present work, the relation between the internal quantum efficiency and carrier concentration for chlorine doped ZnSe layers grown on GaAs substrates are discussed for the first time.

2. EXPERIMENTAL

ZnSe epitaxital layers were grown by atmospheric MOCVD on semi-insulating GaAs substrates. The source materials were dimethylzinc and dimethylselenide. Hydrogen chloride gas was also introduced into the reactor to obtain an n-type layer.

Luminescence efficiency was measured at room temperature under different excitation conditions. An He-Cd laser was used for lower excitation levels than 10^{22} e/h pairs cm^{-3} sec^{-1} and a cathode ray was used for higher excitation levels than 10^{22} e/h pairs cm^{-3} sec^{-1}. ZnSe luminescence inensity was compared with green LED emission, for which the external efficiency was known.

The inernal quantum efficiency was calculated from the luminescence efficiency. A carrier diffusion model in one direction was employed. The carrier concentration dependence of emission efficiency was compared under a moderate excitation density of 10^{23} e/h pairs cm^{-3} sec^{-1}, which is the usual excitation intensity in a LED

3. CALCULATION

Figure 1 shows a schematic diagram for carrier diffusion. The light incidence to ZnSe layer generates carriers in the light penetrating layer. These carriers diffuse inside the layer and make a radiative recombination.

The carrier distribution function is described as follows[4].

$$p-p_0=\frac{I_0(1-R)\tau_h}{\alpha^2 L_h^2-1}\left\{\frac{L_h+S_hL_h/D_h}{1+S_hL_h/D_h}\exp(-x/L_h)-\exp(-\alpha x)\right\} \quad (1).$$

Where α is the absorption coefficient at the illuminated light wavelength, S_h is the surface recombination velocity, τ_h, D_h and $L_h=\sqrt{D_h\tau_h}$ are hole lifetime, diffusion constant and diffusion length, respectively, and x is the distance from the surface. Then, the luminescence intensity I and external quantum efficiency η_{ex} are denoted as follows.

$$I=(1-R)\int_0^{\infty}\frac{p-p_0}{R}\exp(-\alpha' x)dx \quad (2).$$

$$\eta_{ex}=I/I_0=\eta'\eta_i\frac{(1-R)^2}{\alpha^2L_h^2-1}\left\{\frac{L_h+S_hL_h/D_h}{1+S_hL_h/D_h}\frac{1}{1/L_h+\alpha'}-\frac{1}{\alpha'+\alpha}\right\} \quad (3).$$

Where α' is the absorption coefficient at the luminescent wavelength, η_i is the internal quantum efficiency and η' is the reducing factor by surface reflection.

The absorption coefficient, the carrier diffusion length, the life time and surface recombination velocity are needed for calculation. η'_i was calculated as 2.2%. The absorption coefficient was measured in the ZnSe epitaxial layer, where the GaAs substrate had been etched off. Figure 2 shows the absorption coefficient for the ZnSe epitaxial layer. The hole diffusion length was measured from the electron acceleration voltage dependence of the electron beam induced current (EBIC) measurement[5]. Figure 3 shows the hole diffusion length vs. carrier concentration in the ZnSe layers. The hole life time was deduced to be about 10^{-8} sec, if the hole mobility was assumed to be 50 cm^2/vs.

Figure 4 shows the luminescence wavelength dependence of the ratio of external quantum efficiency to internal quantum efficiency. The external quantum efficiency depends on the surface recombination velocity and diffusion length. In ordinary semiconductors, the surface recombination velocity is in the range from 1 to 10^2 m/s. The external quantum efficiency is in the range between 0.5% and 1% of the internal quantum efficiency at the blue emission wavelength, and in the range between 0.9% and 2% at the yellow emission wavelength.

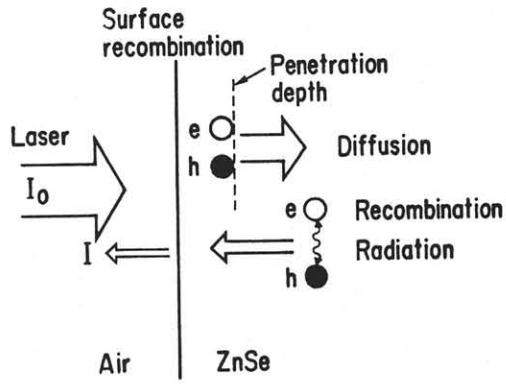

Fig.1 Schematic Diagram for Carrier Diffusion Generated by Incident Light

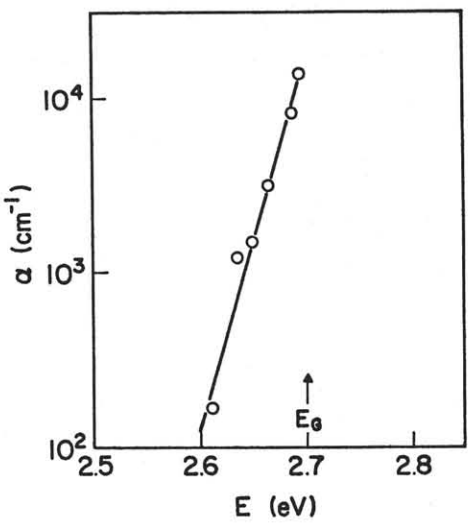

Fig.2 Absorption Coefficient vs. Energy of Light for MOCVD Grown ZnSe Layer

4. RESULTS AND DISCUSSION

Figure 5 shows the photoluminescence spectrum for a chlorine doped ZnSe epitaxial layer, grown where the VI-II ratio was 0.9. Blue luminescence dominated in a low VI-II ratio condition. The blue luminescence wavelength was considered to be from donor-to-band recombination. Table 1 shows the external quantum efficiency for various carrier concentrations, deduced from the luminescence by He-Cd laser excitation. The internal quantum efficiency was calculated from the method mentioned in the previous discussion. The internal quantum efficiency at a low excitation intensity of the ZnSe with 2.1×10^{17} cm^{-3} carrier concentration was in the range between 1.5% at S_h 1m/s and 2.5% at S_h 100 m/s. The actual surface recombination is thought to be high, because the surface becomes nonstoichiometric after growth. Then, the internal quantum efficiency is thought to be near 2.5%.

Figure 6 shows a typical excitation intensity dependence of the internal quantum efficiency. The internal quantum efficiency for blue luminescence is proportional to the excitation intensity in the range from 10^{22} to 10^{23} e/h pairs.cm^{-3} sec^{-1}, and it stays constant in other regions. The internal quantum efficiency at the high excitation region is 10 times larger than that at the low excitation region. On the other hand, The yellow SA luminescence efficiency is constant in the all excitation region.

Figure 7 shows the carrier concentration dependence of internal quantum efficiency at moderate excitation intensity. The error bars in the figure show the calculation errors, because the surface recombination velocity is unknown. As previously discussed, the actual internal efficiency is thought to be near the upper end of the bars. The internal quantum efficiency for blue luminescence is

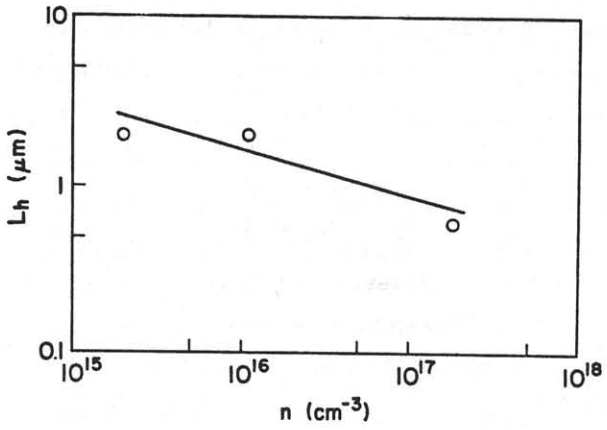

Fig.3 Minority Carrier Diffusion Length vs. Carrier Concentration in Cl Doped ZnSe Layer

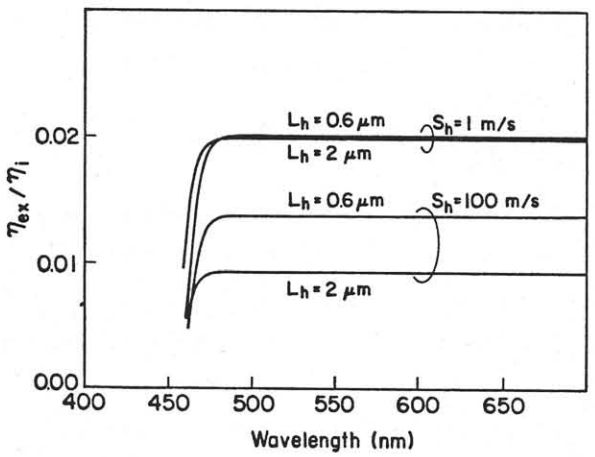

Fig.4 External Quantum Efficiency Ratio vs. Luminescence Wavelength

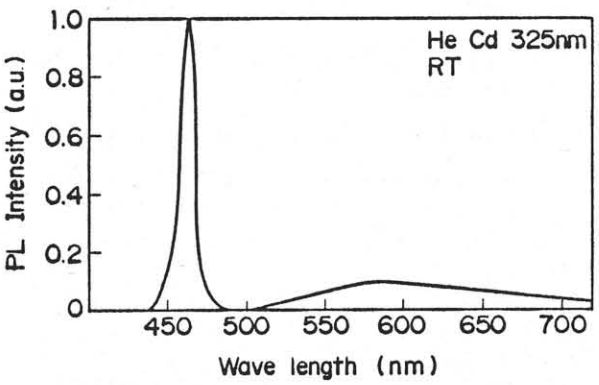

Fig.5 Cl Doped ZnSe Photoluminescence Spectrum Excited by 10 mW He-Cd Laser

proportional to carrier density. This result indicates that the number of non-radiative centers stays constant with increasing carrier intensity, because the radiative center is thought of as a donor, which is proportional to carrier density. Then, the non-radiative centers may not depend on the doping process, but growth conditions. However, the yellow luminescence efficiency depends on carrier density non-linearly. This shows that the SA centers increase with the doping process.

The maximum internal quantum efficiency for blue luminescence was about 25% (external quantum efficiency 0.16%) at $10^{17}/cm^{-3}$ carrier density. This value is sufficient for a practical LED, but slightly lower than the usual value in III-V semiconductors.

5. CONCLUSION

The carrier density dependence for an internal quantum efficiency in ZnSe epitaxial layer was measured for the first time. The internal quantum efficiency was proportional to carrier density. The number of non-radiative centers is not thought to increase with doping, since the SA center slightly increases with doping.

The maximum internal quantum efficiency was 25% (external quantum efficiency 0.16%) for the sample with 2×10^{17} cm^{-3} carrier density at a modest 10^{23} e/h pairs cm^{-3} sec^{-1} excitation intensity, which is the same intensity as for usual LED excitation. This value is sufficient for a practical blue LED.

References

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Table 1 External Quantum Efficiency in Various ZnSe Layers

Specimen No.	Carrier Conc.	External Quantum Efficiency (%)	
		Blue Region	Yellow Region
A	9.7×10^{15}	0.0006	0.002
B	2.0×10^{16}	0.001	0.003
C	2.1×10^{17}	0.016	0.12

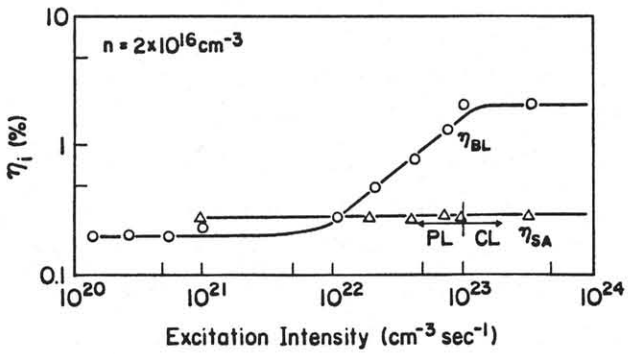

Fig.6 Internal Quantum Efficiency vs. Excitation Intensity

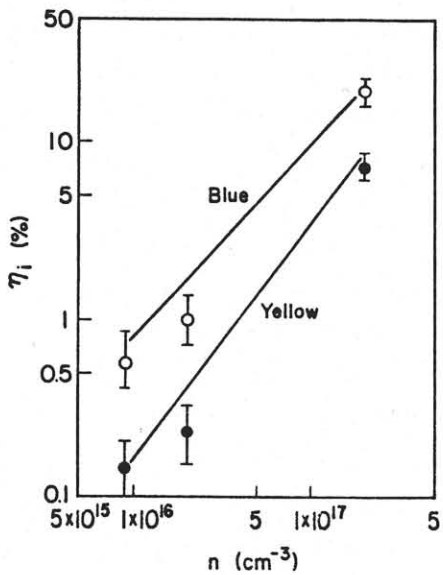

Fig.7 Internal Quantum Efficiency vs. Carrier Concentration in ZnSe Grown Under the Same Condition