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Deep Level Characterization for Aluminum Doped ZnSe Grown by MOCVD

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Deep levels in ZnSe:Al/GaAs grown by MOCVD were studied using deep level transient spectroscopy and photoluminescence. Four electron traps were observed by DLTS with activation energies of 0.5, 0.7, 0.8 and 1.1 eV. The concentration of the deeper electron trap increases relatively with increasing Al concentration. SA centers measured by PL were also influenced by growth conditions. Optimum growth conditions and a proper concentration of Al doping should suppress these deep level formations.

1 Introduction

Zinc selenide, Zinc sulfide and their mixed crystal ZnSSe have attracted much attention as suitable materials for efficient blue emitting devices. These have also been expected to be advantageous materials for mass-production because they can be grown on large area wafers of III-V compound semiconductors,GaAs or GaP.

Recently, crystallinity of ZnSe and/or ZnSSe on III-V semiconductor substrates has been evaluated by means of X-ray diffraction(1,2) and transmission electron microscope(TEM)(3) observation. It has been clear that high concentration macro defects, such as stacking faults and twin boundaries, were observed. It has also been clarified that lattice matching was necessary for improving crystal quality.

Point defects, such as zinc, sulfur, selenium vacancies and complex centers have been studied by means of photoluminescence(4), electron spin resonance(5), deep level transient spectroscopy(6)(7) and so on. Several electron traps in ZnSe were observed at about 0.3-0.8 eV below the conduction band edge, and the SA center was detected near 0.7 eV above the valence band. There are few reports, however, which discuss the correlation between deep levels and intentional doping conditions.

MOCVD, which succeeded in III-V device applications, is regarded as thermally non-equilibrium condition growth and is expected to suppress self-compensation and native defect formation.

In the present work, the authors have studied deep level formation due to intentional aluminum doping into ZnSe, which is grown on GaAs by MOCVD, by DLTS and PL measurement.

2 Experimental

2-1 MOCVD growth

The growth system used in the present work was applicable to a pressure range from 50 mtorr to atmospheric pressure, It consisted of a vertical quartz reactor. A substrate on a SiC coated graphite susceptor was heated by IR-radiant heaters. Dimethylzinc(DMZn) was used as a zinc source and dimethyl selenide(DMSe) or hydrogen selenide(H_2Se) as a selenium source. Triethylaluminum(TEAl) was used as an Al source.

The TEAl flow rate was varied for growths using DMZn and DMSe, and the other growth conditions were fixed. Typical growth parameters are listed in Table 1.

Table 1 Typical growth conditions

	Atmospheric-MOCVD DMSe + DMZn	Low-pressure MOCVD H_2Se + DMSe
[Se] (mole/min)	3.02×10^{-5}	1.56×10^{-4}
[Zn] (mole/min)	1.54×10^{-5}	2.57×10^{-5}
[Aℓ] (mole/min)	$(3.02-15.1) \times 10^{-8}$	7.55×10^{-8}
VI/II	2	6
Tg (°C)	500	340
Pg (Torr)	760	0.1

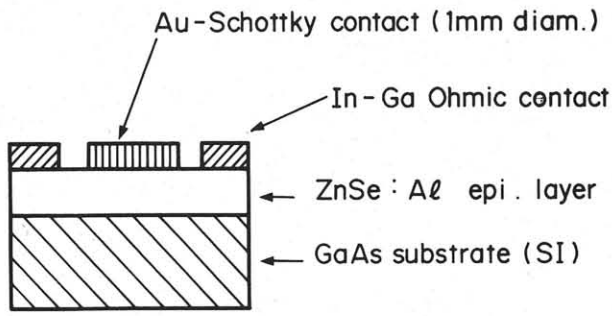

Fig.1 DLTS sample configuration

2-2 Characterization

DLTS spectra were measured by fabricating a Schottky barrier diode, which was made by forming both a 1 mm-diameter Au dot and a In-Ga ohmic contact on the same plane of the grown layer, as is shown in Fig. 1. The measurements were carried out by using a system which is essentialy the same as described by Lang[8].

PL spectra were measured under He-Cd laser excitation.

3 Results and Discussion

3-1 Deep levels of DMSe and DMZn system

Typical DLTS spectra for atmospheric MOCVD grown ZnSe:Al are shown in Fig. 2. The characteristics for these samples are shown in Table 2. Four electron traps were observed, the activation energies of which were calculated to be approximately 0.5, 0.7, 0.8 and 1.1 eV from the conduction band edge. Shallower electron traps dominated in the low Al concentration sample. On the other hand, the deeper electron trap concentration increased relatively with increasing Al concentration. It has been revealed that not only a shallow donor level but also deep electron traps are formed by adding Al donor impurity.

Table 2 Characteristics for atmospheric MOCVD grown ZnSe:Al

[TEAℓ]/[DMZ]		6.6×10^{-4}	2.0×10^{-3}	3.3×10^{-3}
van der Pauw	n [cm^{-3}]	3.9×10^{16}	7.7×10^{17}	1.7×10^{17}
van der Pauw	μH [cm^2/V.sec]	420	320	240
van der Pauw	ρ [Ω.cm]	0.4	0.03	0.2
Trap Level [eV]	0.4	small	—	—
Trap Level [eV]	0.6	large	small	—
Trap Level [eV]	0.8	trace	medium	small
Trap Level [eV]	1.1	—	large	large
SIMS [ppm]		3.5	175	300

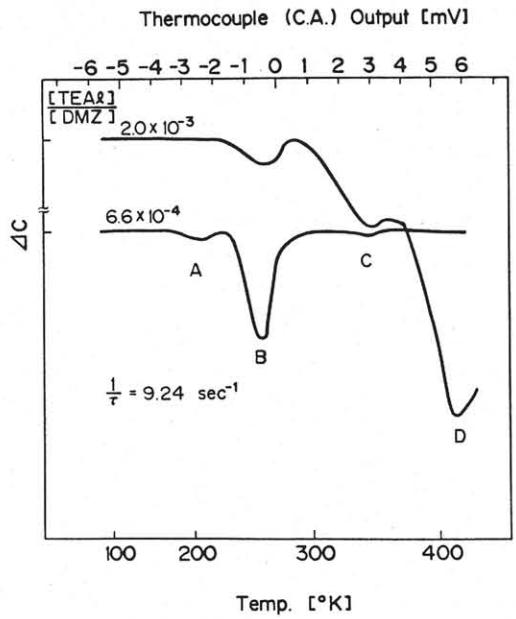

Fig.2 Typical DLTS spectra for ZnSe:Al/GaAs grown by atmospheric MOCVD

Figure 3 shows the Al doping effect on room temperature PL intensity and carrier concentration. The variation of blue PL intensity against Al concentration was quite similar to that of electron carrier concentration. However, red emission intensity increased monotonically with Al concentration.

As shown in Table 2, total Al concentrations were measured by SIMS analysis. The difference between total Al concentration and carrier concentration([Al]-n) increased according to the Al doping condition.

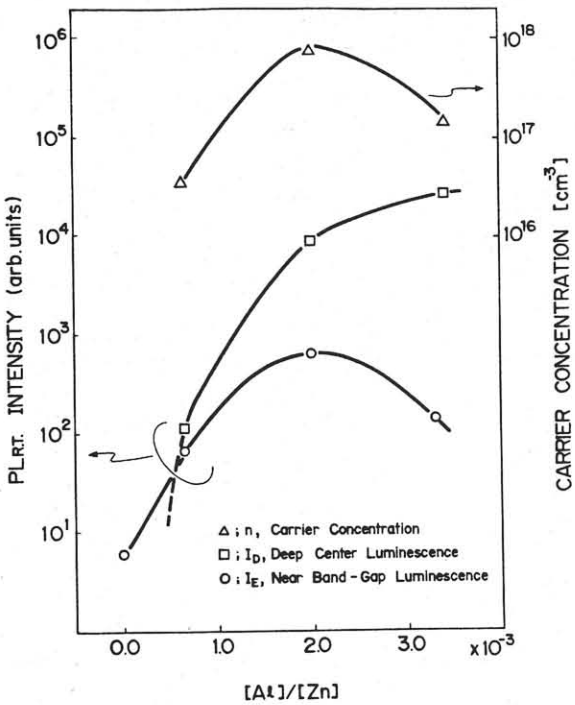

Fig.3 Variations of room temperature PL intensity and carrier concentration vs. Al doping condition

In the present work, there are two possibilities for the origin on red emission at about 2 eV, as shown in Fig. 4. One is SA emission which is considered to originate from electron transition from a shallow donor level to an SA center. The SA emission intensity is also considered to be proportional to the concentration of electrons bounded to shallow donor levels and that of SA centers. The second is the transition of an electron from trap B, near 0.7eV below the conduction band, to a valence band free hole. This bound to free emission intensity may be proportional to the concentration of trap B.

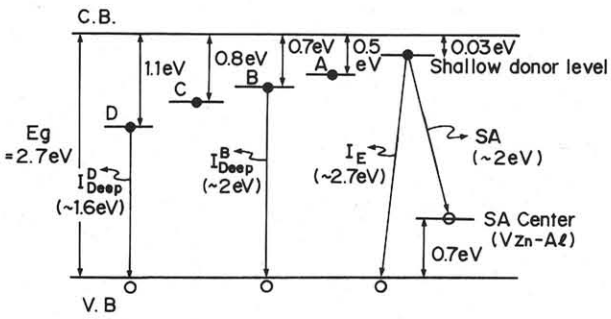

Fig.4 Schematic representation for radiative recombination process

Furthermore, as shown in Fig.5, the Hall mobility decreased with decreasing temperature in the low temperature region in heavily doped samples. As mobility is dominated by ionized impurity scattering, the decrease in mobility with increasing Al concentration in the low temperature region corresponds to the increase in ionized impurity concentration. From the above results, the increase in deep emission intensity with increasing Al concentration may be considered to correspond not to an increase of deep electron traps but to that of SA centers.

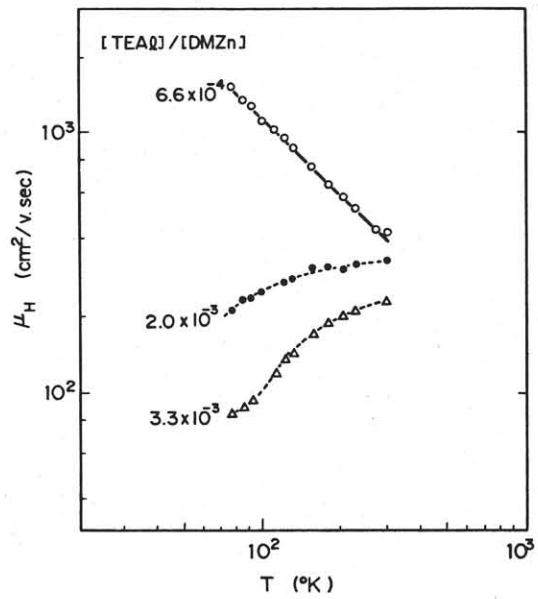

Fig.5 Temperature dependences of Hall mobilities for ZnSe:Al/GaAs grown by atmospheric MOCVD

3-2 Deep levels of H_2Se and DMZn system

A typical DLTS spectrum is shown in Fig.6. Being different from the previous section, trap A and C did not appear. Accordingly, trap A and C are considered to originate from impurities in the Se source material or to be induced by a growth mechanism in the DMSe+DMZn system.

Deep electron trap concentration increased with increasing Al concentration. The growth temperature dependences of PL intensity, carrier concentration and trap concentrations are represented in Fig.7. Blue emission and red emission showed reverse dependence on growth temperature, that is, blue emission intensity has a maximum at about 340°C, though red emission intensity has a minimum at about 340°C.

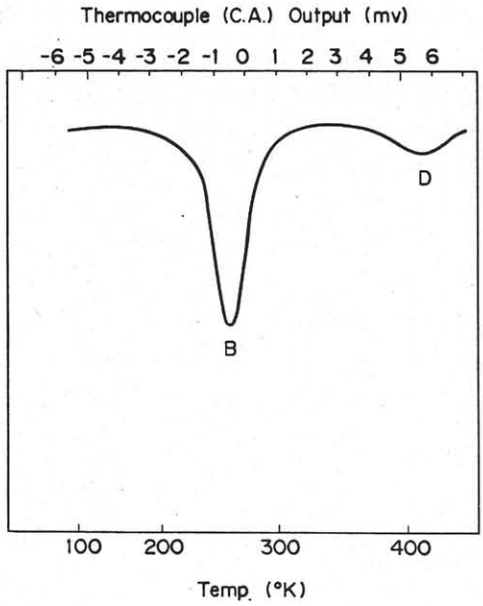

Fig.6 Typical DLTS spectrum for ZnSe:Al/GaAs grown by low-pressure MOCVD

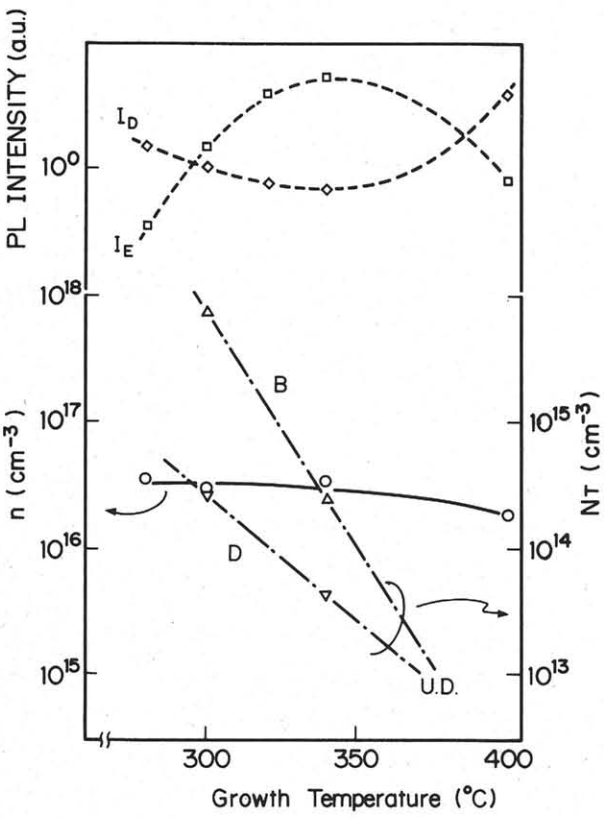

Fig.7 Growth temperature dependence for carrier concentration, trap concentration and PL intensities

On the other hand, deep electron trap concentrations decreased with the increase of growth temperature. These results seem to indicate a possibility of suppressing both deep electron traps and SA centers.

As a result, for the purpose of carrier concentration control and obtaining intense blue emission, it is necessary to improve the crystallinity of epi-layers and to activate Al donors by choosing proper growth conditions and optimizing Al concentration.

4 Summary

Deep level transient spectroscopy was carried out for ZnSe:Al/GaAs grown by MOCVD. Four electron traps were observed with activation energies ranging from 0.5-1.1eV. The concentration of a deeper electron trap increase relatively with increasing Al concentration. SA centers which originate red emission were strongly influenced by Al concentration and growth conditions.

These deep levels are considered to be suppressed by optimization of growth and Al doping conditions.

5 References

(1) A.Kamata,et al., Extended Abstract of the 17th Conf. on SSDM p.233 (1985)

(2) H.Mitsuhashi, et al., Jpn.J.Appl.Phys., 24, L864, (1985)

(3) F.A.Ponce, et al., Thin Solid Films, 108, 133, (1983)

(4) T.Taguchi and T.Yao, J.Appl.Phys., 56, 3002, (1984)

(5) K.M.Lee,et al., Solid State Commun., 35, 527, (1980)

(6) Y.Shirakawa and H.Kukimoto, J.Appl.Phys., 51, 5859, (1980)

(7) P.Besomi and B.W.Wessels, J.Appl.Phys., 53, 3076, (1982)

(8) D.B.Lang, J.Appl.Phys., 45, 3023, (1974)