

Low-Resistivity Cl-Doped ZnSe Layers Grown by Molecular Beam Epitaxy

K.Ohkawa, T.Mitsuyu and O.Yamazaki

Central Research Laboratories
Matsushita Electric Industrial Co., Ltd.
Osaka 570, Japan

Chlorine-doped ZnSe on (100)GaAs has been grown for the first time by Molecular Beam Epitaxy. The Cl-doped ZnSe layer exhibited extremely low resistivity and high carrier concentration compared with Ga-doped ZnSe. Strong blue near-band-gap photoluminescence at room temperature was observed for an appropriate doping level. It was found by SIMS analysis that the diffusion of Cl atoms in the ZnSe layer during growth was negligible.

1. Introduction

ZnSe, with its direct band-gap around 2.7eV at room temperature, is an important material for the candidate of efficient blue light-emitting diodes (LED's). The molecular beam epitaxy (MBE) is one of the most promising techniques for the growth of high-quality ZnSe epilayers¹⁾. It has been found that undoped ZnSe grown by MBE with high-purity source materials shows high electrical resistivity²⁾. In order to obtain n-type ZnSe with low resistivity, doping of Ga has been attempted so far by MBE^{1),3),4)}. However, the carrier concentration and the resistivity have been limited to $5 \times 10^{17} \text{ cm}^{-3}$ and 0.05ohm.cm, respectively.

Recently, we have grown Cl-doped ZnSe layers by MBE using ZnCl_2 as a doping source. The Cl atom doped in ZnSe is known to act as a donor whose ionization energy is 26.2meV⁵⁾. As a result, we have obtained n-type layers with extremely low resistivity. In addition, blue photoluminescence (PL) intensity has considerably improved comparing to our Ga-doped samples. In this paper we report the electrical and PL properties of the Cl-doped ZnSe with various doping levels, and consider the validity of Cl-doped ZnSe for LED's.

2. Experimental procedure

The MBE growth was carried out on semi-insulating (100)GaAs substrates using source materials of Zn, Se and ZnCl_2 under ultra high vacuum conditions. The substrate was chemically etched in a solution of $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 5 : 1 : 1$ at 50°C for 2 minutes. Prior to growth, the substrate was thermally cleaned at 600°C for 10 minutes. The purity of Zn and Se was 6-nine grade, and that of ZnCl_2 was 5-nine grade. Typical source temperatures were 440 and 240°C for Zn and Se, respectively. The beam flux ratio of Zn to Se was kept at about $J_{\text{Zn}}/J_{\text{Se}}=1$. The doping level of Cl was controlled by the temperature of ZnCl_2 (T_{Cl}) in the K-cell. The temperature of ZnCl_2 was varied from 150 to 250°C. In this condition, it is estimated that ZnCl_2 vapor pressure in the K-cell varies from 2×10^{-6} to 1×10^{-3} Torr. The substrate temperature during the growth was 325°C. The growth rate of ZnSe was kept at 2Å/sec, and the layer thickness was around 2 microns.

PL measurements were made at room temperature using 365nm emission from an Hg-lamp as an excitation source. The excitation power density was as low as 0.5 W/cm^2 . Electrical properties were measured by the Van der Pauw method using In-Hg ohmic electrodes.

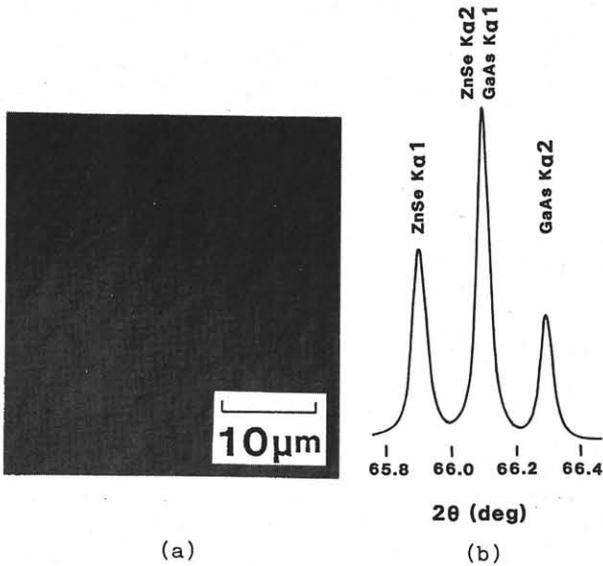


Fig. 1

(a) Nomarski microphotograph of the surface of the Cl-doped ZnSe layer grown at $T_{Cl}=200^{\circ}\text{C}$.
 (b) X-ray diffraction pattern for (400) reflection from Cl-doped ZnSe with 2.0 micron thick grown at $T_{Cl}=200^{\circ}\text{C}$ on a GaAs substrate.

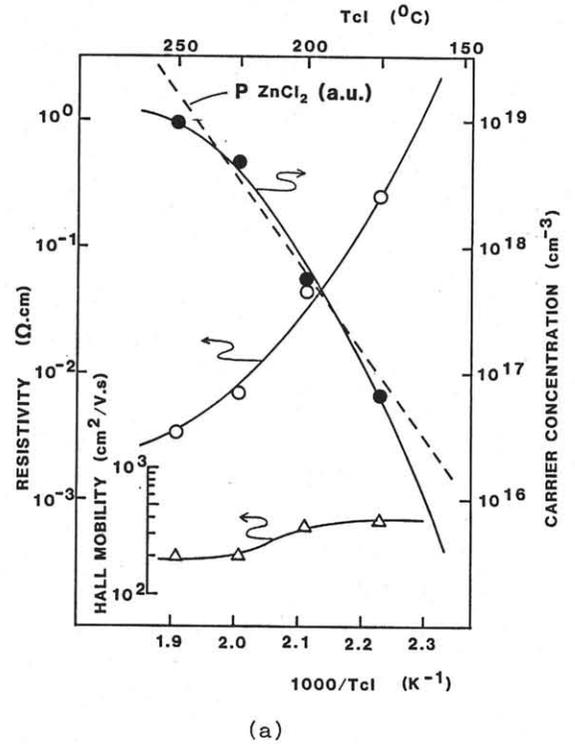
3. Morphology and crystallinity

The Cl-doped ZnSe layers exhibited mirror-like surface morphology for the unaided eye even in the highest doping level. Figure 1(a) shows a Nomarski Microphotograph of a Cl-doped ZnSe layer grown at $T_{Cl}=200^{\circ}\text{C}$. The photograph shows that the surface is slightly wavy. Such morphology was similarly observed in undoped ZnSe layers.

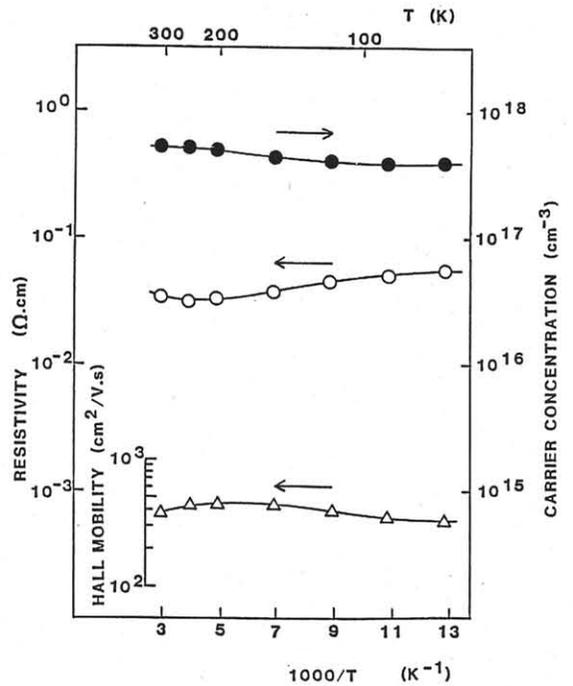
It has been found by X-ray diffraction measurements that the Cl-doped ZnSe layers have good crystallinity regardless of a doping level. Figure 1(b) shows an X-ray diffraction pattern of the Cl-doped ZnSe layer. The peak of ZnSe (400) is as sharp as that of GaAs (400) and its half width is about $180''$. This value is determined by the limit of the instrument.

4. Electrical properties

Our undoped ZnSe layers exhibited high resistivity above 10^4ohm.cm . It has been found that the electrical properties of Cl-doped ZnSe layers can be widely controlled by the ZnCl_2 cell temperature. Figure 2(a) shows the electrical properties of the Cl-doped ZnSe layers at room



(a)



(b)

Fig. 2

(a) Electrical properties of the Cl-doped ZnSe layers at room temperature as functions of T_{Cl} .

(b) Temperature dependence of electrical properties of Cl-doped ZnSe layer grown at $T_{Cl}=200^{\circ}\text{C}$.

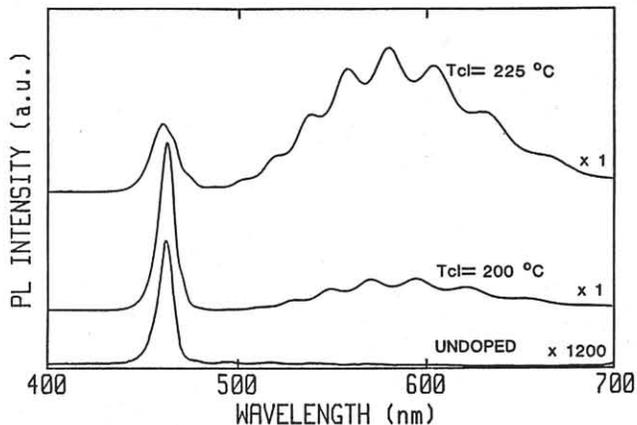
temperature plotted as functions of T_{Cl} . The carrier concentration increases with an increase of T_{Cl} and well corresponds to the $ZnCl_2$ vapor pressure shown in the figure with a broken line. At $T_{Cl}=250^\circ C$ the carrier concentration and the resistivity reach $1 \times 10^{19} cm^{-3}$ and $3 \times 10^{-3} ohm.cm$ respectively; these are remarkable improvements comparing to the Ga-doped MBE ZnSe previously reported⁴). Although the carrier concentration shows a tendency to saturate at $T_{Cl}=250^\circ C$, some improvement would be expected for higher doping level. The Hall mobility is in the range from 200 to $400 cm^2/V.sec$. There is a tendency that the Hall mobility decreases in higher doping levels.

Figure 2(b) shows temperature dependences of the electrical properties of the ZnSe layer grown at $T_{Cl}=200^\circ C$. At room temperature, the resistivity, carrier concentration and Hall mobility are $3.5 \times 10^{-2} ohm.cm$, $5.4 \times 10^{17} cm^{-3}$ and $350 cm^2/V.sec$, respectively. It is found that the carrier concentration is almost independent of temperature, indicating a characteristic of a degenerate semiconductor. The mobility is almost independent of temperature and somewhat decreases in the low temperature region due to the impurity scattering. For lower doping level, remarkable improvement of the Hall mobility was observed at low temperature region.

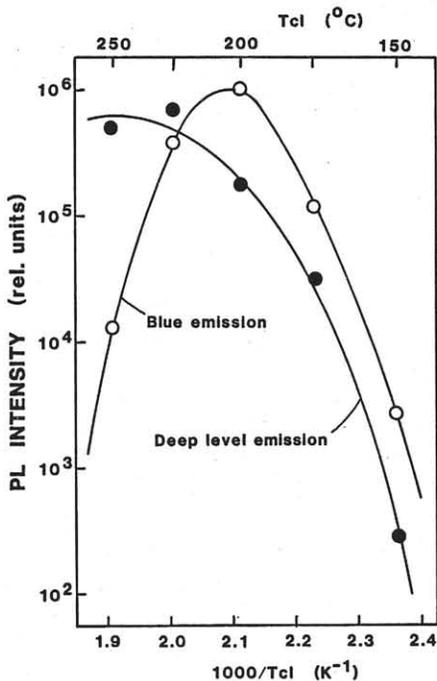
5. Photoluminescence properties

PL spectra of the undoped and Cl-doped layers at room temperature are shown in Fig.3(a). The undoped layer exhibits blue near-band-gap emission around 461 nm. For the Cl-doped layer grown at $T_{Cl}=200^\circ C$, the blue emission significantly increases; the intensity is 1600 times greater than that of the undoped layer. For $T_{Cl}=225^\circ C$, however, broad deep-level emission around 580nm increases and overcomes the blue emission. The peak intensity of the blue emission and that of the deep-level emission are plotted in Fig.3(b) as functions of T_{Cl} . The blue emission is strongest at $T_{Cl}=200^\circ C$, where the deep emission is in an allowable level. This intensity of blue emission is four times larger than that of our Ga-doped ZnSe grown at the optimum condition⁴).

It is obvious that this doping level is optimum for active layers in LED's, while the higher doping level is useful for n^+ contacting layers which minimize the series resistance of the devices.



(a)



(b)

Fig. 3

(a) PL spectra of the undoped and Cl-doped ZnSe layers at room temperature.

(b) Peak intensity of the blue and deep-level emission as functions of T_{Cl} .

6. SIMS analysis

A sample having a structure shown in Fig.4(a) was analyzed by SIMS. At first a highly doped n^+ layer ($T_{Cl}=250^\circ\text{C}$) was grown on a GaAs substrate. Then T_{Cl} was rapidly decreased to 200°C without interruption of the growth and an n layer was grown. Finally, the cell shutter was closed and an undoped ZnSe layer was grown. The thickness of each layer was similarly about 0.6 micron.

The SIMS analysis was carried out using Cs^+ primary ions. Figure 4(b) shows the in-depth profiles of ^{35}Cl , ^{75}As and $^{141}\text{ZnSe}$ in this sample. The boundary between the GaAs substrate and the ZnSe layer is observed very clearly. It seems that mutual diffusion of these elements scarcely occurs at the growth temperature. The boundary between the n and n^+ layers is not so sharp because of the transition of T_{Cl} during growth. However, the boundary between the n and undoped layers is very sharp. This result means that Cl atoms in the ZnSe layer scarcely diffuse at the growth temperature, i.e. 325°C .

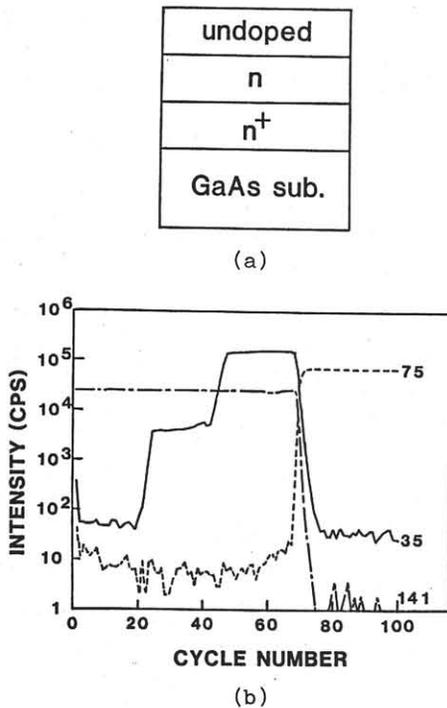


Fig. 4

(a) Structure of the sample for SIMS analysis. The thickness of each layer is about 0.6 micron.

(b) In-depth profiles of ^{35}Cl , ^{75}As and $^{141}\text{ZnSe}$ by SIMS analysis.

It is found that the ratio of Cl concentration in the n^+ layer to that in the n layer is about 30. On the other hand, the ratio in carrier concentration should be 18 according to the results shown in Fig.2(a). This fact means that a considerable amount of Cl atoms in the n^+ layer is inactive. The inactive Cl atoms seems to relate to the origin of the deep-level emission.

7. Conclusion

Epitaxial layers of Cl-doped ZnSe were grown on GaAs substrates by MBE using ZnCl_2 as a doping source. The layers showed mirror-like morphology and good crystallinity as well as undoped layers. The strongest blue photoluminescence was obtained at $T_{Cl}=200^\circ\text{C}$, where the resistivity and carrier concentration were $3.5 \times 10^{-2} \text{ohm.cm}$, $5.4 \times 10^{17} \text{cm}^{-3}$, respectively. For a higher doping level, the carrier concentration attained to $1 \times 10^{19} \text{cm}^{-3}$, which is suitable for n^+ contacting layers. It was found that the diffusion of Cl atoms in the ZnSe layer was negligible at the growth temperature.

We conclude that Cl is more suitable than Ga as an n -type dopant in MBE ZnSe for blue LED's. The strong ionicity of Cl may provide higher doping efficiency.

Acknowledgement

We are grateful to Y.Yoshioka and M.Sato of Matsushita Technoresearch, Inc. for their contribution to SIMS analysis.

References

- 1) T.Yao: J. Cryst. Growth 72 (1985) 31-40.
- 2) K.Yoneda, Y.Hishida, T.Toda, H.Ishii and T.Niina: Appl. Phys. Lett. 45 (1984) 1300.
- 3) T.Niina, T.Minato and K.Yoneda: Jpn. J. Appl. Phys. 21 (1982) L387.
- 4) K.Ohkawa, T.Mitsuyu and O.Yamazaki: Extended Abstracts (The 33rd Spring Meeting, 1986); The Japan Society of Applied Physics and Related Societies, 1a-Y-3,4.
- 5) R.N.Bhargava: J. Cryst. Growth 59 (1982) 15.