Extended Abstracts of the 1992 International Conference on Solid State Devices and Materials, Tsukuba, 1992, pp. 330-332

Invited

Doping and MBE Growth of ZnSe for Blue LEDs and LDs

Kazuhiro OHKAWA, Ayumu TSUJIMURA, Shigeo HAYASHI
Shigeo YOSHII and Tsuneo MITSUYU

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

Highly-conductive n- and p-type ZnSe layers have been successfully grown by MBE with Cl doping and nitrogen radical doping techniques, respectively. Carrier scattering mechanism and compensation in MBE-grown ZnSe layers have been studied by optical and electrical measurements. It was found that electron scattering at 77 K was dominated by neutral impurity scattering. The self-compensation effect has not been observed for both n- and p-type ZnSe layers.

1. Introduction

Blue light-emitting diodes (LEDs)[1] and blue-green laser diodes (LDs)[2-4] made from ZnSe-based pn junction have been demonstrated recently. Doping of ZnSe is the key technology to fabricate these devices.

Column-III donors such as Al and Ga were generally used to obtain n-type ZnSe layers up to 1985.[5,6] Electron concentration of these layers was limited to the order of 10^{17} cm^{-3}. We have paid attention to column-VII elements as n-type dopant, and succeeded, for the first time, in the growth of high-quality n-type ZnSe with strong band-edge photoluminescence (PL) emission and electron concentration greater than 10^{18} cm^{-3}.[7] We have employed $ZnCl_2$ as Cl source in molecular beam epitaxy (MBE).

With respect to p-type doping, many attempts were made to incorporate acceptors into ZnSe. We have reported in 1990, for the first time, the successful p-type doping, then reproducible p-type ZnSe layers are obtainable.[8] We named it "Nitrogen radical doping". Hole concentration of N-doped ZnSe layers exceeded 10^{17} cm^{-3}.[9] Nitrogen responsible for doping is an excited nitrogen molecule at $^3\Sigma_u^+$ state.[8,10] An $N_2(^3\Sigma_u^+)$ molecule is dissociated into N atoms on ZnSe surface.[11]

In this paper, we report on new interpretation of electron transport in n-type ZnSe layers, and on electrical compensation in n- and p-type ZnSe layers.

2. Compensation and electron transport in Cl-doped ZnSe layers

Cl-doped ZnSe layers were grown by MBE using Zn, Se and $ZnCl_2$. Electron concentration was controlled by $ZnCl_2$ cell temperature (T_{Cl}=150 - 250 °C). Electron concentration was in the range from 10^{16} to 10^{19} cm^{-3} at 300 K. Dominant peak in excitonic PL emission for Cl-doped ZnSe layers is neutral-Cl-donor bound exciton emission (I_2) as shown in Fig.1. PL measurement was performed at 4.2 K using a He-Cd laser (325 nm, 0.5 W/cm^2). I_2 emission shifts toward higher energy at the heavier doping level (higher T_{Cl}) together with asymmetric broadening with tail extending to lower energy. These phenomena are remarkable for the samples having the electron concentration greater than that of Mott transition, i.e., N_M=5.6x10^{17} cm^{-3}. Using Hanamura's theory[12], the spectrum of I_2 emission can be simulated by taking the ionized impurity concentration (N_i) as an adjustable parameter. As is seen in the figure, the fit is quite satisfactory. The values of N_i determined are 5.5x10^{17}, 3.0x10^{18} and 1.0x10^{19} cm^{-3} for samples with T_{Cl}=200, 225 and 250 °C. These N_i are in good agreement with electron concentration at 4.2

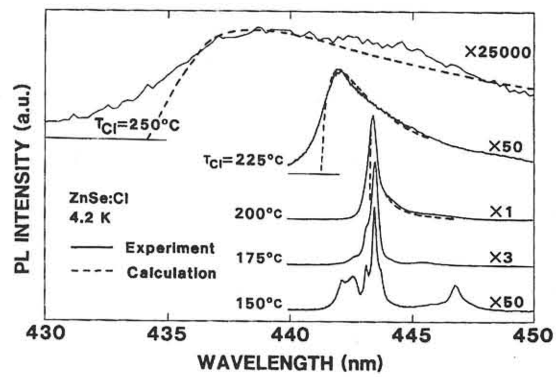

Fig.1 PL spectra measured at 4.2 K for Cl-doped ZnSe/GaAs with various doping levels. Dashed lines show calculated line shapes of I_2 emission.

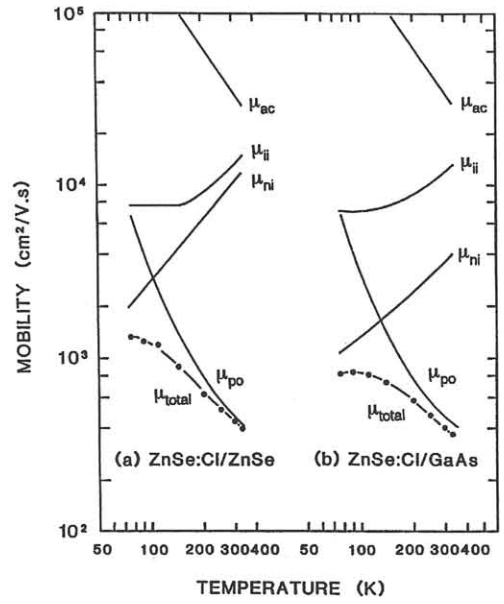

Fig.2 Temperature dependence of electron mobility for Cl-doped ZnSe homo and heteroepitaxial layers. Dots are experimental values, and solid lines are calculations.

K. This result shows the equation of

$$N_i = N_D^+. \quad (1)$$

This equation means the electrical compensation in n-type ZnSe is negligible. The self-compensation effect was not observed for MBE-grown Cl-doped ZnSe layers. The compensation calculated from Ruda's theory[13] is 0.6–0.9 for our Cl-doped ZnSe layers. Such high compensation was not observed. We must reconsider electron transport which is the base of Ruda's theory.

Figure 2 shows temperature dependence of Hall mobility of experiments and calculations. Samples are Cl-doped ZnSe homo and heteroepitaxial layers with the same doping level n_{300K}=6x10^{16} cm^{-3} and mobility μ_{300K}=400 cm^2/(Vs). The total mobility μ_{total} including all major scattering mechanisms is approximately

$$\mu_{total}^{-1} = \mu_{po}^{-1} + \mu_{pe}^{-1} + \mu_{ac}^{-1} + \mu_{ii}^{-1} + \mu_{ni}^{-1} \quad (2)$$

where μ_{po} is polar optical phonon scattering, μ_{pe} is piezoelectric phonon scattering, μ_{ac} is acoustic phonon scattering, μ_{ii} is ionized impurity scattering and μ_{ni} is neutral impurity scattering. Ionized impurity is only ionized Cl donors as described in Eq.(1). Neutral impurity consists of neutral-Cl-donors and lattice defects. Temperature dependence of electron concentration are the same in both layers in Fig.2. Thus the scatterings except μ_{ni} must have the same values in both layers. Ruda's theory can not explain the difference in mobilities for these layers at 77 K. The difference is originated from lattice defects, since crystallinity of homoepitaxial layers is better than that of heteroepitaxial layers. Neutral impurity scattering due to lattice defect is presumably an

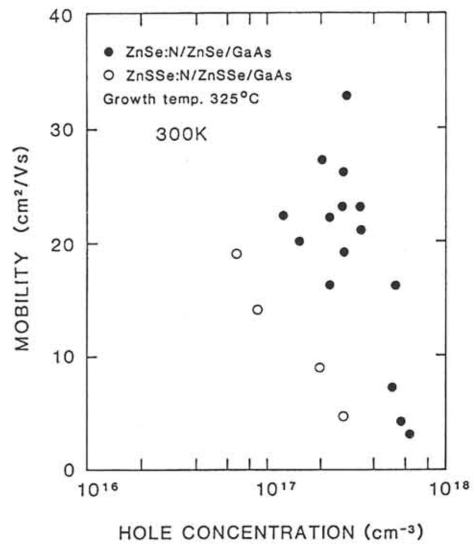

Fig.3 Free-hole concentration and mobility for N-doped ZnSe and ZnSSe layers on GaAs substrates at 300 K.

inherent character for wide band-gap II-VI compounds, since lattice defects are easily generated by large ionicity.

3. Compensation in N-doped ZnSe layers by radical doping

Incorporation of N acceptors into ZnSe was made by radical doping during MBE growth. $N_2(^3\Sigma_u^+)$ radical beam is generated from an RF discharge plasma cell. Figure 3 shows electrical property of N-doped ZnSe and ZnS_xSe_{1-x} (X=0.07) layers on GaAs. The property was measured by means of Hall effect at 300 K. High-resistivity undoped ZnSe and ZnSSe layers (about 1 μm) were introduced in between p-type layers and GaAs substrates. Temperature during MBE growth of these samples is 325 ˋC. Hole concentration in both ZnSe and ZnSSe exceeded 1x10^{17} cm^{-3}. Hall mobility depends on N doping level; mobility decreases with increasing hole concentration. Mobility for ZnSSe is degraded by the alloy scattering.

P-type ZnSe:N layers by radical doping have good optical property. Acceptor-related emissions are observable even at room temperature. Strong donor-acceptor pair emission (DAP) was observed at 12 K as shown in Fig.4. Relative intensity of recombination emission between a free electron and an acceptor hole (FA) to DAP emission increased with increasing temperature. Dominant DAP emission at 12 K suggests the existence of donors. Ionization energy of the donor is as deep as about 50 meV calculated from peak energy of DAP emission. Such a deep donor is unknown so far, since ionization energies of column-III and VII donors are in the range of 25–29 meV.

Nitrogen concentration ([N]) was evaluated

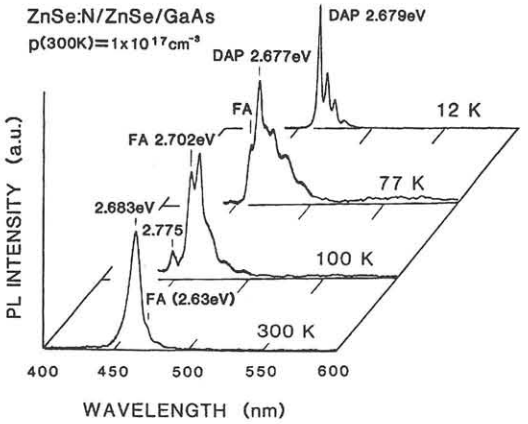

Fig.4 PL spectra for an N-doped ZnSe layer at various temperature.

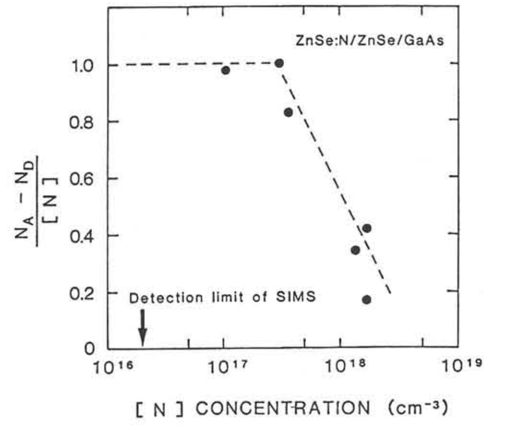

Fig.5 Ratio of net acceptor concentration to [N] at various [N].

by secondary ion mass spectrometry (SIMS). Detection limit of N is as low as $2x10^{16}$ cm^{-3} by using CsN signal. To our knowledge, this is the smallest detection limit ever reported on SIMS analyses in N. Figure 5 shows that net acceptor concentration (N_A-N_D) from capacitance-voltage (C-V) measurement has the same value of [N] below [N]=$3x10^{17}$ cm^{-3}. Electrical compensation has not been detected in this analysis. The former analysis of DAP emission showed the existence of deep donors which is, however, observable below 100 K. Thus optical and electrical results suggest that a center acts as a deep donor at low temperature, but it does not act as donor at room temperature. Further study is necessary to understand the center in p-type ZnSe:N. The ratio of (N_A-N_D)/[N] decreases above [N]=$3x10^{17}$ cm^{-3}. Interstitial N probably increases, since crystallinity of N-doped ZnSe degraded with increasing [N] as shown in Ref.14.

4. Conclusion

The analysis of I_2 emission from Cl-doped ZnSe layers indicates that the ionized impurity concentration is in good agreement with ionized-Cl-donor concentration, meaning compensation in MBE-grown Cl-doped ZnSe to be negligible. The study of electron transport has shown that main electron scattering at 77 K is not due to ionized impurity but due to neutral impurity. Neutral impurity scattering due to lattice defect is presumably an inherent character for wide band-gap II-VI compounds. Free hole concentration for both N-doped ZnSe and ZnSSe layers by radical doping exceeded $1x10^{17}$ cm^{-3}. Deep donor with ionization energy 50 meV was observed in optical measurement. Electrical measurement has shown, however, that electrical compensation in p-type ZnSe:N is negligible. Compensation including the self-compensation effect was not observed in both MBE-grown n- and p-type ZnSe layers.

Acknowledgement

We greatly acknowledge H.Takeishi of Kagoshima Matsushita Electronics Co., Ltd. for his valuable contribution, and F.Toujou of Matsushita Technoresearch, Inc. for SIMS analysis.

References

1) K. Ohkawa, A. Ueno and T. Mitsuyu, in Extended Abstr. 1991 Int. Conf. on Solid State Devices and Materials, Yokohama, 1991, p.704.
2) M.A.Haase, J.Qiu, J.M.DePuydt and H.Cheng, Appl.Phys. Lett. 59(1991) 1272.
3) H.Jeon, J.Ding, W.Patterson, A.V.Nurmikko, W.Xie, D.C. Grillo, M.Kobayashi and R.L.Gunshor, Appl.Phys.Lett. 59 (1991) 3619.
4) S. Hayashi, A. Tsujimura, S. Yoshii, K. Ohkawa and T.Mitsuyu, unpublished.
5) W. Stutius, J. Appl. Phys. 53(1981) 284.
6) T. Niina, T. Minato and K. Yoneda, Jpn. J. Appl. Phys. 21 (1982) L387.
7) K. Ohkawa, T. Mitsuyu and O. Yamazaki, in Extended Abstr. 1986 Int. Conf. on Solid State Devices and Materials, Tokyo,1986, p.635; J.Appl.Phys. 62(1987)3216.
8) K. Ohkawa, T. Karasawa and T. Mitsuyu, PIII-21 in Abstr. 6th Int. Conf. on Molecular Beam Epitaxy, San Diego, August, 1990; J. Cryst. Growth 111(1991) 797.
9) K. Ohkawa, A. Ueno and T. Mitsuyu, Jpn.J.Appl.Phys. 30 (1991) 3873.
10) K. Ohkawa, A. Ueno and T. Mitsuyu, J.Cryst.Growth 117 (1992) 375.
11) T. Nakao and T. Uenoyama, in Extended Abstr. 1992 Int. Conf. on Solid State Devices and Materials, Tsukuba, 1992.
12) E. Hanamura, J. Phys. Soc. Jpn. 28(1970) 120.
13) H.E. Ruda, J. Appl. Phys. 59(1986) 1220.
14) K.Ohkawa, T.Karasawa and T.Mitsuyu, Jpn.J.Appl.Phys. 30(1991) L152.