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Extremely Low Resistivity, High Electron Concentration ZnSe Grown by Planar Doping Method

Z. Zhu, H. Yoshihara, K. Takebayashi and T. Yao

Department of Electrical Engineering, Hiroshima University,

1-4-1, Kagamiyama, Higashi-Hiroshima 724, Japan

The n-type ZnSe with electron concentration up to $3x10^{20}$ cm^{-3} and low resistivity down to $1x10^{-4}$ Ωcm has been grown using a planar doping technique of chlorine during molecular beam epitaxy. The photoluminenscence evaluation shows that the planar doped ZnSe layers are superior to uniformly doped ones especially for the case of high Cl-doping. The in-depth profile of Cl concentration in a planar doped sample was measured with a secondary ion mass spectroscopy (SIMS). The SIMS analysis shows only slight diffusion of the incorporated Cl atoms even in highly doped samples.

1. INTRODUCTION

Growth of bipolar conductive ZnSe with extremely low resistivity and high carrier concentration are requisite to achieve cw operation of a blue laser diode at room temperature[1,2]. So far, nitrogen[3], lithium[4] and chlorine[5] have been found to be promising p- and n-type dopants for ZnSe respectively, whereas other dopants of group I, V, III and VII elements have resulted in poor electrical and optical properties. However, there seems to be an upper limit on the attainable net acceptor or net donor concentrations. The upper limits of the carrier concentration have been estimated to be $1x10^{18}$ cm^{-3} for nitrigen[2], $1x10^{18}$ cm^{-3} for lithium[4] and $1x10^{19}$ cm^{-3} for chlorine[5]. In the case of lithium, one of the main causes is due to the compensation related to the formation of lithium interstitials[6], while in the case of nitrogen, the compensation due to nitrogen associated donors is considered to be responsible for the net acceptor concentration limit[3]. However, we have successfully overcome this difficulty by employing atomic-layer doping technique of lithium in Li-doped ZnSe[7]. It is believed that the compensation for n-type ZnSe would be due to the formation of deep defects such as SA centers. In the case of chlorine[5], the net donor concentration increases proportionally with the concentration of incorporated chlorine up to 10^{19} cm^{-3}, while it tends to saturate and eventually begins to decrease when the Cl concentration exceeds $1x10^{19}$ cm^{-3}. It is necessary to develop a well controlled doping process in order to overcome the compensation.

The planar-doping technique has been attempted to attain higher carrier concentration than that achieved by uniform doping technique. This technique has been recently applied to Ga- and Li-doping during MBE of ZnSe[7,8]. deMiguel, et. al. have reported the enhancement of the doping efficiency when Ga is introduced on Zn stabilized ZnSe surface[8]. Using the planar-doping method, the carrier concentration in the 10^{18} cm^{-3} range has been achieved, which is several times larger than that of Ga-doped ZnSe grown by uniform doping during MBE. High quality p-ZnSe layers with hole concentrations above $3x10^{17}$ cm^{-3} have been grown using the planar doping technique of lithium during MBE[7]. The hole concentration obtained is several times larger than that of Li-doped ZnSe grown by uniform doping during MBE. In the case of Li-doping, Li is introduced on a Se stabilized ZnSe surface. This letter reports the growth and characteristics of heavily doped n-type ZnSe layers with chlorine by the planar-doping method, Using this method, high quality ZnSe layers with high electron concentration up to $3x10^{20}$ cm^{-3} and low resistivity down to $1x10^{-4}$ Ω cm have been obtained. This result shows remarkable improvement in electrical properties by one order of magnitude or more in comparison with the uniformly doped samples or n-type ZnSe grown by any other doping methods reported so far.

2. EXPERIMENTAL

The planar-doping growth was carried out with a conventional MBE using the sources of Se, Zn and $ZnCl_2$. Prior to planar doping, a ZnSe buffer of about 6000Å was deposited onto a (001)GaAs substrate. Planar doping was achieved by incorporating Cl on spatially separated atomic sheets during the MBE growth of ZnSe. The doping level of Cl was controlled by Cl-cell temperature or the ratio of impingement time of Cl to the growth time of ZnSe. The surface crystallinity of Cl-doped ZnSe during growth was examined by *in situ* observations of RHEED patterns. For high Cl-doping above the concentration of $1x10^{19}$ cm^{-3} , the RHEED shows a distinct (2x1) streaky pattern during planar doping, while it shows an enlonged (2x1) spotty pattern

during uniform doping. This fact indicates that the surface crystallinity of the planar doped sample is superior to that of the uniformly doped sample. The continuous supply of high concentration of Cl atoms during uniform doping would result in a deviation of ZnSe from stoichiometry, which may lead to the degradation of surface morphology. On the other hand, in the case of planar doping, the surface morphology would be recovered during the periods of the undoped ZnSe growth.

3. RESULTS AND DISCUSSION

The in-depth profile of Cl concentration was measured with a secondary ion mass spectroscopy (SIMS) as shown in Fig.1. The sample structure prepared for SIMS measurements is shown in the upper part of Fig.1. The Cl dopant was spatially incorporated in between ZnSe space-layers of 400Å. The times for Cl doping were respectively 100, 50, 20, 10, and 5 seconds, which correspond to the growth of Cl-doped ZnSe of 80, 40, 16, 8 and 4Å. During Cl doping period, growth of ZnSe was not interrupted. The substrate temperature was 350°C, and the flux ratio of Zn to Se was less than but very close to unity. The Cl-cell temperature was kept at 180°C. The growth rate was determined by measuring the period of the RHEED oscillations during growth of the ZnSe buffer layer. As seen from Fig.1, the incorporated Cl atoms are confined in the Cl-doped region, indicating only slight diffusion of Cl atoms in ZnSe at temperature of 350°C. The half-width of the Cl-doping profile is estimated to be 120Å, and the Cl concentration in undoped ZnSe regions due to thermal diffusion from Cl-doped region is on the order of 10^{16} cm^{-3}. As the time for Cl doping decreases, the Cl concentration in the region of Cl-doped ZnSe decreases, and the peak concentration of Cl doping profile is approximately proportional to the opening time of the Cl-cell shutter.

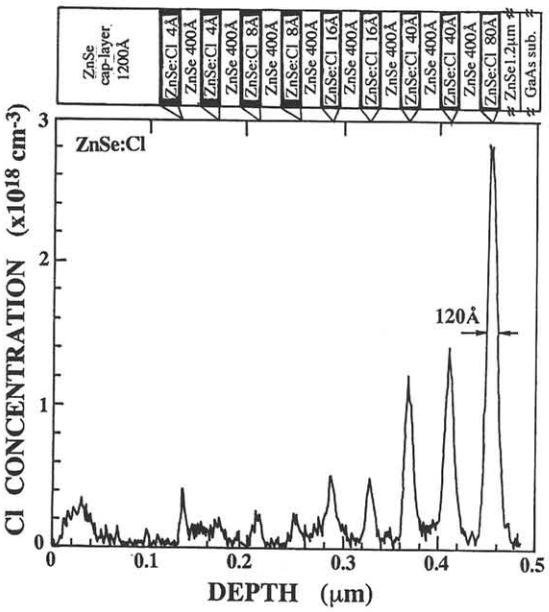

Fig.1 The SIMS depth profile of Cl atoms in the planar doped ZnSe sample. The structure of the sample is schematically shown in the upper part of the figure.

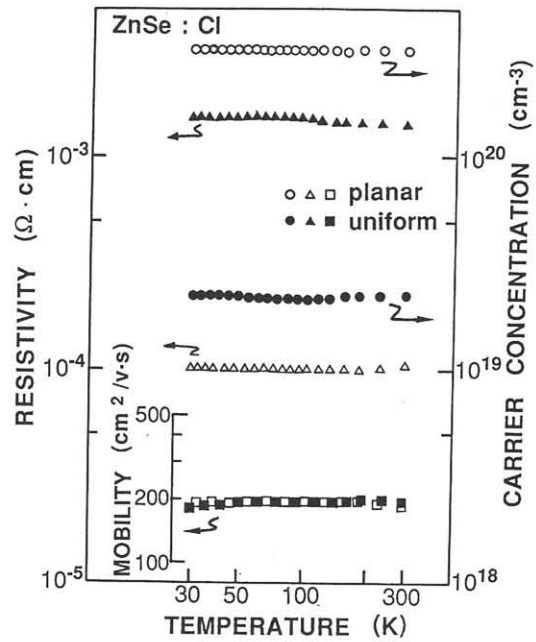

Fig.2 Temperature dependence of electrical properties of the Cl-doped ZnSe layers grown by the planar doping and uniformly doping techniques respectively.

The samples were electrically characterized by the van de Pauw method. The dots of gallium-indium alloy were annealed at 300°C for 30 seconds in a nitrogen gas atmosphere to obtain ohmic contacts. Fig.2 shows the electrical properties of Cl-doped ZnSe layers in a temperature range from 30 to 300K. The data represented by hollow marks are obtained from the planar doped sample with the Cl-doping period of 12Å separated by a ZnSe spacing layer of 78Å. The total number of the period was 40. The substrate temperature was kept at 350Å and the Cl-cell temperature was at 230°C. The growth was carried out under a Se-rich condition but very near to the stoichiometric condition. The growth rate of Cl-doped ZnSe was evaluated to be 0.6 A/s from RHEED oscillation. The filled marks, for comparison, represent the results from the uniform doped sample grown under the same growth condition, i.e., the same Se-, Zn-, Cl-cell and substrate temperatures with that for the planar doped sample. The values of the electron concentration and resistivity of the planar doped sample attain $3x10^{20}$ cm^{-3} and $1x10^{-4}$ Ωcm, respectively. This result shows remarkable improvement in electrical properties by one order of magnitude or more in comparison with the uniformly doped samples or n-type ZnSe grown by any other doping methods ever reported[5,8,9,10]. The hall mobilities obtained from both the planar doped and uniformly doped samples are measured to be about 200 cm^2/vs. The electrical properties are independent of temperature due to high concentration of electron.

The photoluminescence (PL) spectrum of the planar doped sample at 4.2K shows a strong excitonic emission (I_2) associated with Cl donors, but the emission bands at 2.0eV related to deep levels dominate the spectrum. The I_2 peak shifts to 2.823eV due to strong screening effect of donor electrons on the bound exciton, which is consistent with the electrical properties. The details of the PL properties will be presented elsewhere.

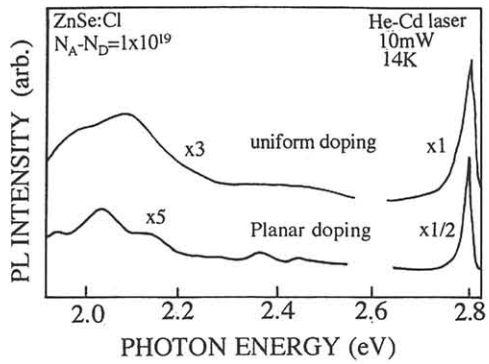

Fig.3 Low temperature photoluminescence spectra for two samples of ZnSe:Cl with the same electron concentration of $1x10^{19}$ cm^{-3} grown by planar doping and uniform doping techniques.

Fig.3 shows PL spectra of the samples with the same electron concentration of $1x10^{19}$ cm^{-3} grown by the planar doping and uniform doping techniques respectively. The planar doped sample consists of undoped ZnSe period of 300Å and Cl-doping period of 10Å. The total number of the period was 20. The substrate temperature was kept at 350°C and the flux ratio of Zn to Se was near to unity for both samples. The Cl-cell temperatures were 210°C for the planar doping and 190°C for the uniform doping. The thickness of Cl-doped ZnSe was about 6200Å for both samples. PL measurements were performed at 14K with a He-Cd laser excitation of 10mW. The excitonic emission associated with neutral donors dominates the spectra for both samples. The intensity ratios of the deep level emission to the excitonic emission are measured to be 1/10 for the planar doped sample and 1/3 for the uniformly doped sample. These results suggest a higher crystalline quality of the planar doped ZnSe layers than that of the uniformly doped layers. This is consistent with the results obtained from the electrical measurements and the RHEED observations.

3. CONCLUSION

We have grown high quality ZnSe layers with high electron concentration up to $3x10^{20}$ cm^{-3} and low resistivity down to $1x10^{-4}$ Ω cm using the planar doping technique. The electrical results obtained from the planar doped samples show great improvement in electrical properties by one order of magnitude or more in comparison with the uniformly doped samples or n-type ZnSe grown by any other doping methods reported so far. The PL results show that the planar doped ZnSe layers have high quality superior to that of the uniformly doped one for high Cl-doping above $1x10^{19}$ cm^{-3}.

The in-depth profile of Cl concentration in a planar doping sample was measured with a secondary ion mass spectroscopy (SIMS). The SIMS analysis shows that the incorporated Cl atoms distribute on spatially separated atomic sheets in ZnSe. The peak concentration of Cl increases with the period for Cl doping.

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