

Molecular beam epitaxial doping of ZnMgSe using ZnCl₂

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In this letter we have investigated the *n*-type doping properties of Zn_{1-x}Mg_xSe grown by molecular beam epitaxy using a solid ZnCl₂ source as dopant. We describe the effect of dopant source temperature on the carrier concentration and show that the optimum doping temperature changes with varying Mg compositions. At the same time, the highest achievable electron concentration decreases as the Mg content in the sample increases, and this behavior can be described by a model that assumes that the Fermi level is pinned 120 meV above the conduction band edge of ZnSe, in an absolute energy scale. © 1995 American Institute of Physics.

Since the demonstration of the ZnSe-based blue-green laser in 1991,¹ most attention has been devoted to pseudomorphic structures on GaAs, using ZnMgSSe quaternary compounds as cladding layers and ZnCdSe or ZnSe in the quantum wells (QW). Recent studies have suggested that the strain in the active zone is responsible for the triangular non-luminescence dark defects that appear during the degradation process and have shown the importance of using unstrained QWs in these devices.² The ternary compound ZnMgSe, with larger band gap and lattice constant, as compared to ZnSe, is an alternative candidate as a base material for lasers with unstrained ZnCdSe in the active zone. We have recently shown that the addition of Mg to ZnSe raises the conduction band edge of the alloy, maintaining the valence band edge constant,³ resulting in a type I band lineup between ZnMgSe and ZnCdSe. On the other hand, there are yet no experimental data on doping of this system. A theoretical study from Chadi,⁴ indicates that it should be *n*-type dopable with Al. In this work, we have chosen ZnCl₂, as the dopant source, since it has been successfully used in ZnSe, leading to electron concentrations as high as $3 \times 10^{20} \text{ cm}^{-3}$.⁵

The samples were grown in a vertical molecular beam epitaxy system, equipped with conventional effusion cells for Zn, Mg, Se, and ZnCl₂. Epi-ready (001) oriented GaAs were used as substrates. The doped ZnMgSe layers were grown on the top of 100 nm thick undoped ZnSe and ZnMgSe buffers. The presence of the thin ZnSe buffer improves the crystalline quality of the subsequent compound layers. The thickness of the doped layer was between 0.5 and 1.5 μm . All layers were grown under slightly Se rich conditions, showing in a (2 \times 1) surface reconstruction in the reflection high-energy electron diffraction patterns during the growth. Although no systematic study has been done, samples grown this way have shown the best doping results, when compared with those grown under Zn stabilized conditions or too much Se overpressure. The substrate temperature was 330 °C for all samples. The Mg content of the samples was determined

from high resolution x-ray diffraction measurements assuming a linear dependence of the lattice constant with Mg concentration. The crystalline quality of the samples, as measured by the width of the rocking curve varies strongly with the total sample thickness. The full width at half-maximum of the (004) reflection changes from more than 1000 arcsec for 0.5 μm thick samples to about 500 arcsec when the thickness is larger than 1.5 μm . The lattice constant for MgSe was assumed to be 5.89 Å.⁶ The van der Pauw method was used for electrical characterization. Ohmic contacts were obtained soldering Au wires with In directly on the top of the layers. The photoluminescence (PL) measurements were performed at 4.2 K using the 368.3 nm line of an Ar laser at 5 mW for excitation.

The effect of the ZnCl₂ source temperature on the obtained electron concentration is shown in Fig. 1 for ZnSe and Zn_{0.64}Mg_{0.36}Se. For ZnSe, the doping concentration increases until it reaches a maximum and then decreases abruptly. The saturation of the carrier concentration in wide gap II–VI semiconductors is a common effect and have been explained to result from some self-compensation mechanism or by achieving the solubility limit.^{7,8} The observed decrease in the electron concentration for higher ZnCl₂ temperatures in our

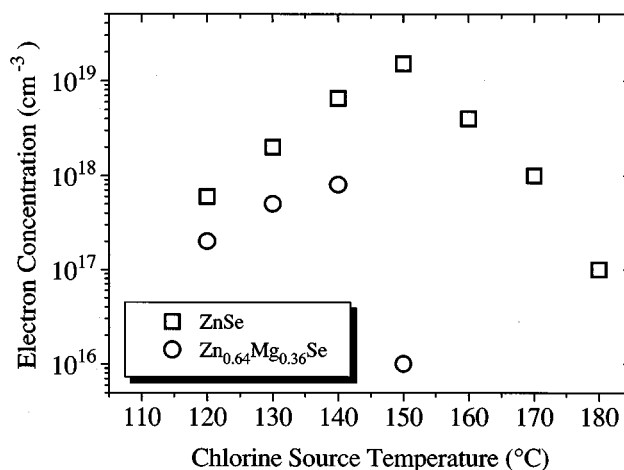


FIG. 1. Electron concentration as a function of the ZnCl₂ source temperature for ZnSe and Zn_{0.64}Mg_{0.36}Se at room temperature.

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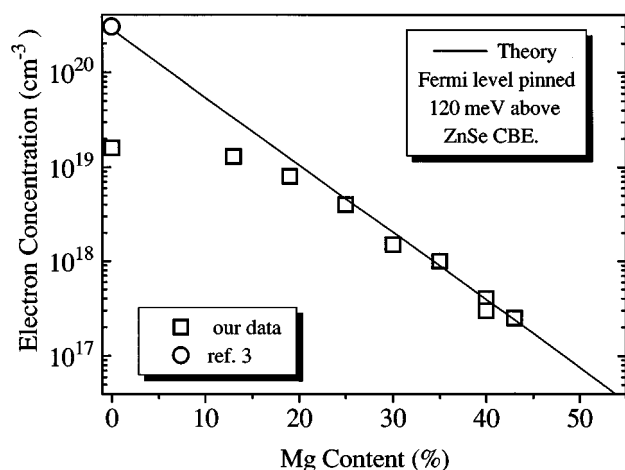


FIG. 2. Electron concentration as a function of Mg content in the alloy. The squares are our data and the circle is the highest electron concentration reported on the literature for ZnSe (Ref. 3). The solid line is calculated assuming that the Fermi level is pinned at a fixed level 120 meV above the ZnSe CBE.

samples indicates, otherwise, the formation of electrically inactive Cl complexes, and has been already reported in the literature.⁹ The further increase of the chlorine temperature produces three-dimensional growth and even reduces the growth rate.

The same behavior is observed for the ZnMgSe ternary layers, with the difference that the maximum electron concentration is lower and is achieved for a lower ZnCl₂ temperature. The lower temperature probably means that the solubility limit of chlorine in ZnMgSe decreases with Mg content. It has been demonstrated, recently, that there seems to be a close relation between the maximum free-carrier concentration and the band edges of a semiconductor in an absolute energy scale.¹⁰ This model suggests that, as long as the compensation mechanism is the same, the Fermi level is pinned to a reference energy level, and the maximum achievable electron concentration is determined only by the energy difference between the conduction band edge (CBE) and this level.

No difference in electron concentration have been measured for ZnMgSe layers with different thickness. Since the thickness is directly related with the crystalline quality of the samples, as discussed above, we can conclude that the crystalline quality has little influence on the achieved carrier concentration.

In Fig. 2, we plot the maximum electron concentration obtained for ZnMgSe as a function of the Mg content. The solid line is calculated assuming an energy gap of 3.6 eV (Ref. 6) for MgSe and a linear change of the CBE with Mg content.³ The Fermi level was assumed to be pinned 120 meV above the CBE of ZnSe, in an absolute energy scale. The use of a lower (higher) value for the pinning energy would just shift down (up) the curve but the slope would remain the same since it is determined only by the variation of the ZnMgSe CBE. This model, using the same pinning level energy, has been used to explain the doping behavior of iodine in CdMgTe,¹¹ indicating the universal character of this "compensation level," in the sense that its position relative

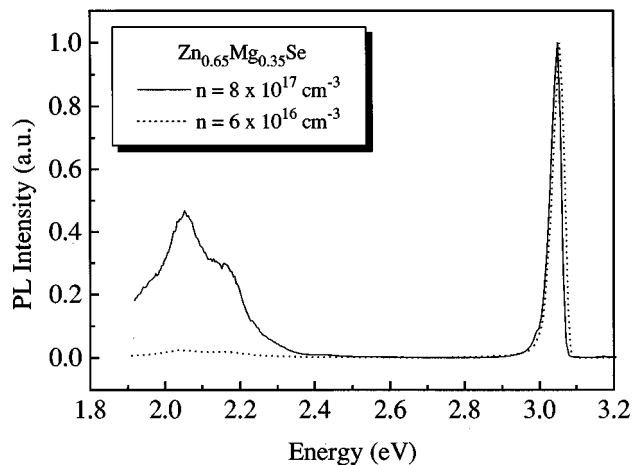


FIG. 3. Photoluminescence spectrum of doped Zn_{0.65}Mg_{0.35}Se samples with electron concentration of $8 \times 10^{17} \text{ cm}^{-3}$ and $6 \times 10^{16} \text{ cm}^{-3}$. The intensity ratios of the excitonic to the deep-level emission are 50 and 2, respectively.

to the vacuum is identical for several compounds and dopants.¹²

The agreement between theory and experimental data is very good for Mg concentration larger than about 20%. For samples with lower Mg content, the measured electron concentrations are smaller than the predicted values. The experimental point marked as a circle in Fig. 2, is the highest electron concentration reported for ZnSe on the literature,⁵ and is fitted well by our model. This stresses that the model gives an upper limit for the concentration and indicates that, for lower Mg contents, our samples show some other compensation mechanism. The sample from Ref. 5 was grown using a so-called selective doping method that should reduce the compensation. We have tried to apply this method to our samples, but no increase in the net carrier concentration or change in the PL spectra was observed.

In Fig. 3 we show the PL spectra of two Zn_{0.65}Mg_{0.35}Se samples doped to $8 \times 10^{17} \text{ cm}^{-3}$ and $6 \times 10^{16} \text{ cm}^{-3}$. The thickness of both samples is about 1 μm . At low doping concentration the PL is dominated by a near band edge emission of an exciton-donor pair. The intensity ratio of the excitonic emission to the deep-level emission at about 2.1 eV is 50. As the electron concentration increases, the deep-level emission increases at the same time that the excitonic emission decreases. The intensity ratio for high doped sample is only 2. The same behavior has already been observed for highly doped ZnSe:Cl samples, and described to be related to the formation of complex centers involving Cl associated with lattice vacancies.⁵ The use of the selective doping method should help to suppress the deep-level emission, but the PL spectra of samples doped using this method have not shown any difference.

We have shown that ZnMgSe can be *n*-type doped with chlorine above 10^{17} cm^{-3} for Mg contents under 45%. The ZnCl₂ source temperature to obtain optimum doping levels decreases with increasing Mg content, indicating a reduction of the solubility limit of chlorine in the ternary mixture. The maximum obtainable carrier concentration can be fitted using a model that assumes the presence of a compensation level in

a fixed energy position, related to the vacuum level, situated 120 meV above the CBE of ZnSe, to which the Fermi level is pinned as soon as sufficient dopant atoms are introduced. The net electron concentration remains constant or even decreases, probably due to formation of electrically inactive complexes or Cl precipitates, if the dopant concentration further increases. These results show that ZnMgSe is a good choice of an alternative base material for blue lasers, employing unstrained ZnCdSe QWs in the active zone. A possible substrate material for these devices could be InP.

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