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Low temperature growth and plasma enhanced nitrogen doping of ZnSe by metalorganic vapour phase epitaxy

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Abstract

The combination of diisopropylselenide (DIPSe) and diethylzinc (DEZn) was used to grow ZnSe by metalorganic vapour phase epitaxy (MOVPE). The results are compared with those obtained from samples grown with diethylselenide (DESe) and DEZn. Furthermore, we analysed the influence of plasma stimulation of DIPSe and DESe, as well as plasma enhanced nitrogen doping. Plasma stimulated growth with DESe at 480°C results in ZnSe which shows resolved free and bound excitons and negligible deep centre emissions in 11 K PL spectra. By using DIPSe without plasma stimulation, the kinetically controlled growth regime was found in the temperature range from 380 to 480°C. In PL only broad distributed emissions from 2.4 to 2.78 eV were observed, arising from impurities in the Se precursor. With plasma enhancement the diffusion controlled growth regime was extended down to 330°C. In the PL spectra, excitonic emissions were found beside the emission band (2.4–2.78 eV). Deep centre emission (2.0 eV) appeared only for $T_D < 360^\circ\text{C}$. Doping experiments were carried out by using plasma precracking of the Se precursor and simultaneously stimulating nitrogen dopant gas in a plasma. The donor–acceptor pair (DAP) emission of the doped layers increases for decreasing growth temperatures (440 to 360°C), if DIPSe and DEZn are used as precursors. Increasing the N_2 flux causes an increasing nitrogen concentration. Samples grown in N_2 carrier gas at 380°C show a maximum measured nitrogen concentration of $1.7 \times 10^{18} \text{ cm}^{-3}$. The layers were highly compensated, due to the impurities in the Se precursor and to additional hydrogen and carbon incorporation.

1. Introduction

For the production of optoelectronic devices, which work on the basis of ZnSe, the control of n- and p-type conductivity is necessary. Many attempts to grow p-type ZnSe failed [1]. p-type conducting ZnSe with a free carrier concentration above $1 \times 10^{18} \text{ cm}^{-3}$ was demonstrated with molecular beam epitaxy (MBE) [2]. However, the physical mechanism of p-type conduction is not

clear yet. For the doping plasma activated nitrogen was used. It is difficult to use elements other than nitrogen for p-type doping, due to several reasons: One problem is the limited solubility of these elements in ZnSe [3]; another problem is the compensation. Lithium shows an amphoteric behaviour, since interstitial lithium acts as a donor and compensates the free holes generated by lithium on zinc sites [4]. The group V elements arsenic and phosphorus create deep centres. A theoretical model proposed by Chadi and Chang explains the compensation mechanism [5]. This theory predicts a reduced existence of deep centres with increasing electronegativity of the dop-

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ing element. Therefore nitrogen is the most useful candidate to achieve p-type conduction. Until now, attempts to achieve p-type doping with other growth methods than MBE result in highly resistive samples or the carrier concentration was very low [6,7]. In MOVPE, NH_3 was used as a doping gas for these attempts [6,7]. Due to the successful doping in MBE technology it should be useful to grow ZnSe:N at low temperatures and to use plasma stimulated nitrogen as well for doping in MOVPE to obtain highly conductive p-type ZnSe . The growth of ZnSe with the combination of DEZn and DESe requires a deposition temperature of at least 480°C [8]; therefore this combination does not seem to be useful for successful doping experiments. Because DEZn is decomposed at 300°C [9], we investigated the growth with and without plasma-cracked DIPSe and DEZn . The combination of diallylselenide and DEZn , investigated earlier [10,11] is not useful in reducing the growth temperature. For comparison we grew samples with the well known precursor combination DESe and DEZn .

2. Experimental procedure

The ZnSe layers were grown in a horizontal MOVPE reactor. The plasma precracking was carried out by a DC plasma source 10 cm in front of the susceptor as reported earlier [11]. As substrate we used (100) GaAs, which was 2° misoriented towards the nearest $\langle 110 \rangle$ direction. The substrates were annealed for one minute at 600°C in a hydrogen atmosphere. DEZn , DESe and DIPSe , which is contaminated with Zn, As, Sn, B, Sr and Te [12], were used as precursors. The vapour pressure of DIPSe ($(\text{C}_3\text{H}_7)_2\text{Se}$) was measured and follows the expression: $\log(p/\text{hPa}) = 8.56 - 2193.1 \text{ K}/T$. Thus, at a bubbler temperature of 17°C the material yields a vapour pressure of 9.9 hPa, which is adequate for MOVPE. For the experiments, the Se partial pressure was set to 2.84 Pa and the VI/II ratio was varied from 0.2 to 12.3. We grew the layers using a total flux of 1.5 SLM of H_2 . The total pressure was 100 hPa in the experiments without plasma enhancement and 20 hPa in experiments with plasma

precracking of the Se precursor. The plasma power was approximately 6 W. For the doping experiments, an additional nitrogen flux of 0.120 SLM was activated in a DC plasma with a power of 5.6 W. For comparison, layers were grown using DESe and DEZn under the same conditions. The epilayers were characterized by photoluminescence (PL) at 11 K, scanning electron-microscopy (SEM), Hall and SIMS measurements. SIMS measurements were carried out with 5.5 keV O_2^+ and Cs^+ primary ion beams. The detection limit was 1×10^{17} for nitrogen, 4×10^{17} for hydrogen and 3×10^{16} atoms cm^{-3} for carbon. A helium-cadmium laser (325 nm) and a 1 m monochromator with a GaAs photomultiplier were used for the PL measurements. The samples were irradiated with a low excitation power ($0.01\text{--}0.5 \text{ W cm}^{-2}$).

3. Growth of ZnSe without plasma

In Fig. 1, the dependence of ZnSe growth rate obtained with different Se precursors on reciprocal temperature is shown. At a total pressure of 100 hPa and a VI/II ratio of 2.1 ($T_D = 480^\circ\text{C}$), we measure a growth rate of $0.48 \mu\text{m/h}$ by using DESe and DEZn as precursors. Below a deposition temperature of 480°C , we found the kinetically controlled growth regime. Decreasing the

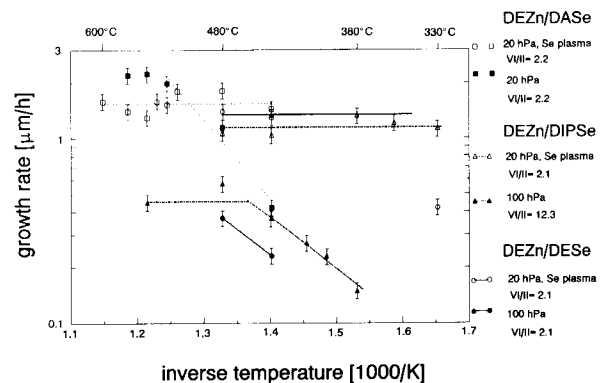


Fig. 1. Growth rate of ZnSe grown with different precursor combinations: DESe , DASE (diallylselenide), DIPSe with DEZn . The filled symbols are results of growth without plasma enhancement and the open symbols are results of plasma enhanced growth.

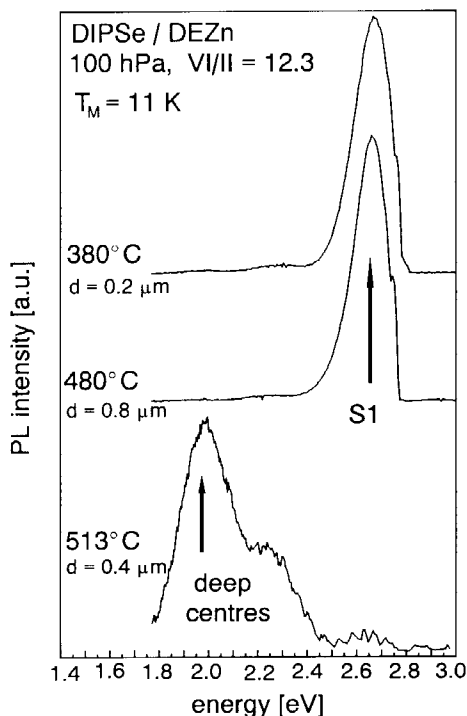


Fig. 2. 11 K PL spectra of layers grown with DIPSe and DEZn ($P_D = 11$ hPa, VI/II = 12.3, without plasma enhancement) in dependence of growth temperature.

growth temperature below 480°C causes a reduction of the PL intensity. This indicates poor crystalline quality for samples grown below 480°C as shown earlier [8].

In growth rate experiments carried out with DIPSe and DEZn at a VI/II ratio of 12.3, we observed the kinetically controlled growth regime up to 480°C. At $T_D = 380^\circ\text{C}$, we found an extremely low growth rate of only 0.2 $\mu\text{m}/\text{h}$. At temperatures higher than 480°C, the diffusion controlled growth regime was found. The growth rate was 0.66 $\mu\text{m}/\text{h}$. The sample surface was mirror-like up to a growth temperature of 400°C. At higher growth temperatures the surface started to get rough. In SEM micrographs (magnification 5000 \times), “pyramids” were observed on the surface. In Fig. 2, the 11 K PL spectra of ZnSe grown with DIPSe without plasma enhancement at different growth temperatures are shown. All PL spectra of samples grown below 500°C are

nearly identical. Only a broad emission band S1 in the energy interval from 2.4–2.78 eV was observed. We correlate this emission band to impurities in the Se precursor. An interpretation as donor–acceptor pair (DAP) luminescence seems to be incorrect, because from time-resolved measurements the decay of this emission is nonexponential in the ns range. We assume that this emission can be interpreted as an exciton bound to a deep centre [13]. Layers which were grown at temperatures higher than 500°C show dominating deep centre emissions at 1.95 and 2.25 eV. In all samples, no excitonic emissions were observed. At $T_D = 480^\circ\text{C}$, the variation of the VI/II ratio from 0.8 to 12.3 has no influence on the PL spectra. Below a VI/II ratio of 0.8, the PL spectra show deep luminescence at 1.74 eV. SIMS measurements show a carbon and hydrogen concentration below the detection limit of SIMS.

4. Growth with plasma enhancement

The dependence of optical properties on growth temperature of ZnSe grown with plasma activated DESe is shown in Fig. 3. If DESe was used as the Se precursor together with plasma enhancement, the so-called copper green (2.25 eV) and self-activated centre emissions (2.0 eV) were reduced compared to non-plasma grown samples. At a growth temperature of 480°C, the samples show dominating resolved excitonic emissions in the PL spectra. The Y-peak at 2.6 eV which is attributed to lattice defects [14], is clearly visible and more enhanced in samples grown at 440°C. Phonon replica of the I_1^{deep} line (2.78 eV) can be detected. Deep centre emissions arise in the PL spectra of ZnSe grown below 440°C. This indicates a distorted lattice structure of ZnSe grown at temperatures below 480°C, although plasma precracking of DESe was used.

By using plasma precracking of the DIPSe precursor, the diffusion controlled growth regime is extended down to 330°C (see Fig. 1). The growth rate was 1.66 $\mu\text{m}/\text{h}$ with a VI/II ratio of 2.1 and at a total pressure of 20 hPa. The surfaces of the samples which were grown below 380°C were smooth in SEM micrographs. Macro-

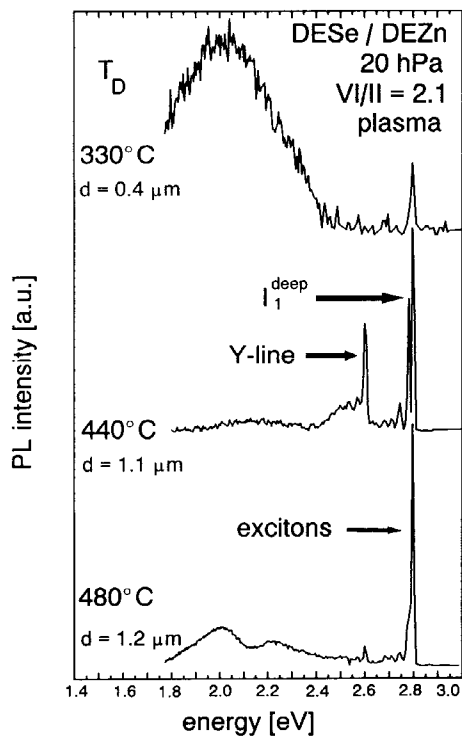


Fig. 3. PL spectra at 11 K of ZnSe samples grown with plasma precracking of DESe.

scopic defects on the surface were observed for epilayers which were grown at temperatures higher than 400°C. Below a deposition temperature of 360°C, deep centre emissions at 2.3 eV dominate in the PL spectra. In the PL spectra of layers grown at T_D higher than 360°C, the emission band S1 with a maximum at 2.65 eV due to the contaminations present in the Se precursor dominates the spectrum. Excitonic emissions of samples grown below 440°C can be resolved. The dominating emission band S1 is present even in samples grown with different VI/II ratios (0.8 to 12.3) and total pressures (20 hPa to 150 hPa). Samples grown with a VI/II ratio of 0.2 show only deep centre luminescence at 1.7 eV. SIMS measurements indicate that the hydrogen and carbon incorporation is below the detection limit of SIMS, comparable to the non-plasma grown samples.

5. Plasma enhanced nitrogen doping of ZnSe

Since free and donor bound excitons of ZnSe, grown with DESe and DEZn at a temperature of 480°C can be resolved, this growth temperature was first used for the doping experiments in spite of the high growth temperature. To increase the growth rate, the DESe was cracked with plasma. In Fig. 4, the PL spectra of ZnSe:N are shown. Fig. 4a shows the PL spectrum of ZnSe:N grown with DESe and DEZn with a VI/II ratio of 3.0. The nitrogen bound excitonic emission I_1^N at 2.79 eV cannot be resolved in the PL spectra, but the DAP emission at 2.7 eV and their phonon replica are observable. The DAP emission has the same energy position as the DAP emission in heavily nitrogen doped layers grown with MOVPE [7], but MBE grown p-type conducting samples show a DAP emission at 2.681 eV [15]. However, different strain magnitudes in the samples have to be taken into account due to different growth

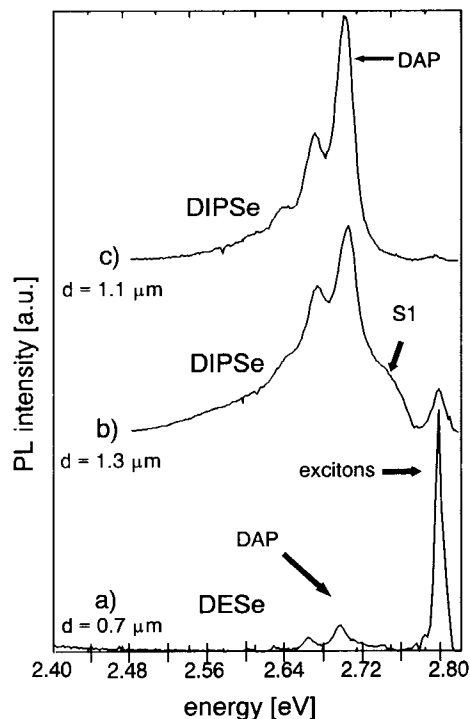


Fig. 4. PL spectra at 11 K of ZnSe:N grown with: (a) DESe, VI/II = 3.0, $T_D = 480^\circ\text{C}$; (b) DIPSe, VI/II = 0.8, $T_D = 380^\circ\text{C}$; (c) DIPSe, VI/II = 0.8, $T_D = 360^\circ\text{C}$.

temperatures and layer thickness. Time resolved PL measurements carried out on samples grown with a VI/II ratio of 3.0 show nitrogen concentrations of $1.5 \times 10^{17} \text{ cm}^{-3}$ [16]. With DIPSe as Se precursor, we reduced the growth temperature down to 360°C for the doping experiments, since at a growth temperature of 480°C and a VI/II ratio (DIPSe/DEZn) of 0.8 no DAP emission of the nitrogen was observed and the PL spectrum was not distinguishable from a PL spectrum of an undoped sample. The PL spectra of DIPSe grown samples doped with nitrogen are shown in Fig. 4b (VI/II ratio = 0.8, $T_D = 380^\circ\text{C}$) and Fig. 4c (VI/II ratio = 0.8, $T_D = 360^\circ\text{C}$). By decreasing the growth temperature to 360°C , the DAP emission of the nitrogen started to dominate the emission band S1 originating from the contamination of the DIPSe. This indicates an increased nitrogen incorporation in ZnSe with a reduced growth temperature. From time resolved PL measurements, a nitrogen concentration of $4.5 \times 10^{17} \text{ cm}^{-3}$ (VI/II ratio = 0.8 at a growth temperature of 380°C) was evaluated. Fig. 5 illustrates the DAP emission of samples grown with different nitrogen fluxes. The nitrogen incorporation can be estimated by the ratio of the intensity of the DAP emission to the intensity of the emission band S1. The shoulder on the high energy side of the DAP emission is clearly visible in Fig. 5. At a growth temperature of 380°C and a VI/II ratio of 0.8 we observed an increased nitrogen incorporation with an increased nitrogen flux as shown. A qualitative estimation is given by the ratio of DAP emission intensity to the excitonic emission intensity, which increases from 4.0 with a nitrogen flux of 34 ml/min to 5.7 at a nitrogen flux of 207 ml/min. All samples were semi-insulating in Hall measurements. To analyse the residual incorporation of extrinsic impurities originating from the growth process such as carbon and hydrogen and the amount of incorporated nitrogen, SIMS measurements were performed. In Fig. 6, a SIMS measurement of a ZnSe sample is shown. This ZnSe stack consists of several layers. The layers labelled (a) and (b) were grown with a VI/II ratio of 0.8 and were doped with plasma activated nitrogen. The layer (c) was grown totally in nitrogen, the hydrogen carrier gas was fully replaced

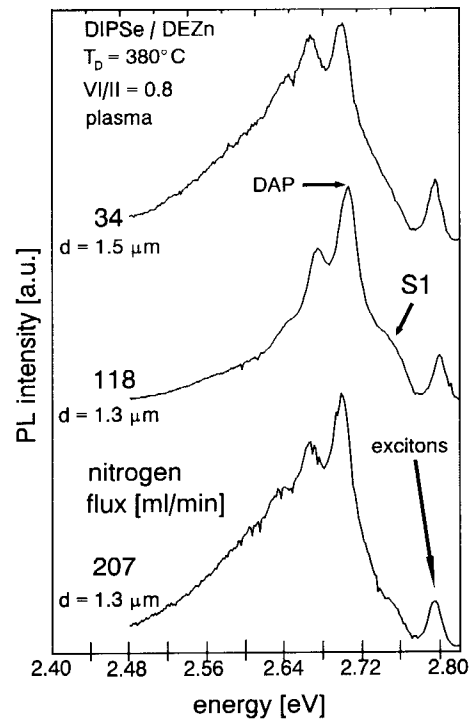


Fig. 5. PL spectra at 11 K of ZnSe:N grown with plasma cracked DIPSe and DEZn with different N_2 doping gas fluxes.

by N_2 , with the same VI/II ratio of 0.8. The other layers are undoped. The growth temperature was 380°C . In layers (a) and (c), the carbon content was approximately $5 \times 10^{17} \text{ cm}^{-3}$ and the

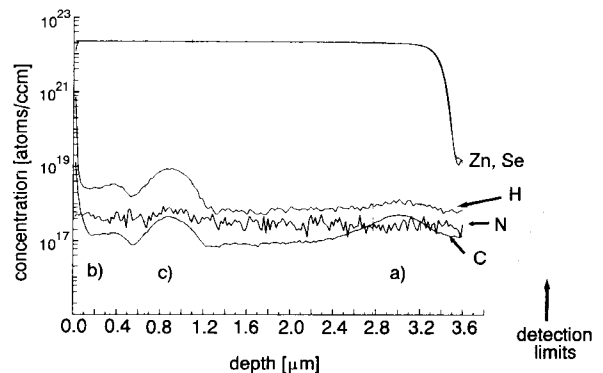


Fig. 6. SIMS measurement of a ZnSe stack: (a), (b) $T_D = 380^\circ\text{C}$, VI/II = 0.8, H_2 as carrier gas, N_2 as dopant gas; (c) like (a) and (b), but nitrogen as dopant and carrier gas.

hydrogen concentration was measured to $1 \times 10^{18} \text{ cm}^{-3}$ for layer (a). In layer (c), we observed a hydrogen concentration of $1 \times 10^{19} \text{ cm}^{-3}$. This shows that the hydrogen originates from the precursors and not from the carrier gas. Time resolved measurements of nitrogen doped layers, grown with nitrogen instead of hydrogen as carrier gas, show a maximum nitrogen content of $1 \times 10^{18} \text{ cm}^{-3}$.

6. Discussion

By using plasma stimulated DESe and DEZn at 480°C the deep centre emission of ZnSe is reduced and free and bound excitons can be resolved. This shows that high quality ZnSe layers can be grown with the plasma MOVPE technique. Furthermore the growth rate is increased with plasma enhanced growth. For the investigated precursor combinations the diffusion controlled growth regime was extended to lower temperatures, for DIPSe/DEZn down to nearly 330°C, as shown in Fig. 1. Plasma enhanced growth results in a sufficiently high growth rate at a low deposition temperature. The emission due to the contamination of the DIPSe prevents the observation of other emissions (e.g., Y-peak, small intensity DAP and excitonic emissions) in DIPSe and DEZn grown samples. The main contamination seems to be tellurium. At a concentration above $2 \times 10^{18} \text{ cm}^{-3}$, this dopant causes exciton trapping and is responsible for the dominating S1 emission band [17], shown in Fig. 2. The absence of deep centre emissions proves that with DIPSe as Se precursor, the growth temperature for ZnSe can be reduced by 100°C in comparison to DESe as Se precursor. The nitrogen incorporation is achieved by plasma MOVPE and can be increased by growth temperature and nitrogen flux. A decrease of the VI/II ratio causes an increase of the nitrogen incorporation, since nitrogen is incorporated on Se lattice sites. Therefore we have three parameters to control the nitrogen incorporation. The choice of an extreme growth temperature (< 360°C, > 500°C; DIPSe) or an extremely low VI/II ratio leads to a deteriorated crystalline quality of the ZnSe:N layers. The

p-type conductivity of nitrogen doped ZnSe is totally compensated by the incorporation of carbon, hydrogen and the Te contamination, which originates from the precursor material. The hydrogen incorporation cannot be reduced by a simple substitution of the hydrogen carrier gas with nitrogen.

7. Conclusion

The optical properties of ZnSe can be improved by using plasma enhanced low pressure MOVPE. The diffusion limited growth regime can be extended to lower deposition temperatures. With DIPSe as Se precursor, a growth temperature of 360°C is suitable for the growth of ZnSe layers with well-resolved excitons in the PL spectra. Plasma activation of N₂ as a dopant gas allows the incorporation of nitrogen up to a concentration of $1.7 \times 10^{18} \text{ cm}^{-3}$, but a parasitic incorporation of carbon and hydrogen occurs. The next steps in investigating p-type conducting ZnSe, grown by MOVPE, should be the avoidance of contaminations in the DIPSe source and the suppression of hydrogen and carbon incorporation into the layers.

8. Acknowledgements

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