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LOW TEMPERATURE GROWTH AND PLANAR NITROGEN DOPING OF ZnSe IN A PLASMA-STIMULATED LP-MOVPE SYSTEM

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ABSTRACT

Ditertiarybutylselenide (DTBSe) and dimethylzinc triethylamine (DMZn(TEN)) were used as precursors for the growth of ZnSe in a low pressure MOVPE process. ZnSe was doped with DC-plasma activated N_2 during the growth process. A planar doping scheme was developped to suppress the hydrogen incorporation into the layers. The emission of donor and acceptor bound excitons in 1.8 K PL spectra was observed. The nitrogen amount in the doped layers can be adjusted by the growth temperature and the N_2 flow into the reactor. Due to the high n-type background carrier concentration of the undoped layers, most of the nitrogen doped layers show n-type conductivity or were semiinsulating. However, some C-V-measurements can be interpreted by p-type conductivity.

I) INTRODUCTION

In order to obtain low-resistivity nitrogen-doped ZnSe samples with metal organic vapour phase epitaxy (MOVPE) it is necassary to grow at low temperatures. High growth temperatures cause intrinsic defects like V_{Zn} or V_{Se} in the layer, resulting in a compensation of the electrical conductivity. However, the reduction of the growth temperature (T_D) leads to an increased incorporation of contaminations, due to increased sticking coefficients. The high concentration of unwanted impurities is one reason for the semiinsulating or n-type behaviour of MOVPE grown samples, emphasizing the importance of the precursor purity. Recently, for precursor combinations with DTBSe growth temperatures lower than 360°C have been demonstrated [1,2]. The MO-source combination DTBSe/DMZn(TEN) allows to grow high-quality ZnSe at temperatures down to 330°C. N-doping of ZnSe during MOVPE growth can be achieved either by a plasma activated nitrogen source [3] successfully employed in MBE techniques or by suitable nitrogen precursors [4]. Independent of the doping technique, nitrogen-doped ZnSe layers grown by MOVPE do not exceed a net-acceptor concentration higher than 2×10^{17} cm^{-3} up to now or they are highly compensated. A major contribution results from incorporated hydrogen, which passivates shallow acceptors [5]. To reduce the incorporation of hydrogen originating from the MO precursors a planar doping technique was investigated, which separates growth and doping phases [6], to avoid reactions of the activated nitrogen with the MO material leading to H incorporation [7]. Similar doping schemes were investigated by MBE technology [8].

The purpose of this work is to investigate the growth of undoped and nitrogen doped ZnSe using the precursor combination DTBSe/DMZn(TEN) and plasma activated N_2 in different doping schemes. The different plasma-doping methods are compared on the basis of results from time-resolved photoluminescence- (PL-), SIMS- and capacitance-voltage (C-V) measurements.

II) EXPERIMENTAL

The DC-plasma reactor was described elsewhere [3]. (100) GaAs substrates, 2° misoriented towards the nearest <110> direction were treated in hydrogen plasma for 2 minutes before growth. Afterwards the surface was stabilized with DTBSe for 2 minutes. Undoped and nitrogen doped ZnSe epilayers were grown at a total reactor pressure of 20 hPa, a VI/II ratio of 0.18, a partial pressure of the Se-precursor of 0.29 Pa, and substrate temperatures between T_D = 300°C and 400°C. Nitrogen doping is performed using a N_2 plasma and different N_2 flow in different doping schemes. In the reactor the MO-precursors and the activated nitrogen are either simultaneously present (homogeneous) or timely separated (planar), therefore thin undoped layers are grown, which are terminated either with Se or Zn. After a short pause, in which the reactor is purged, the nitrogen flow is introduced into the reactor. This sequence was repeated several hundred times to get samples with a thickness of approximately 1μm.

III) RESULTS AND DISCUSSION

The PL of undoped ZnSe samples grown at temperatures between 315 and 400°C is dominated by excitonic recombinations. The samples show deep centre luminescence around 2.0 eV, which is about 100 times weaker than the excitonic recombination and shows no significant dependence on the growth temperature below 400°C. Practically no DAP recombination is observable. But samples grown at 300°C show dominating DAP emission as well as weak excitons and deep-centre luminescence. Comparing the excitonic spectra, it is obvious that not the layer quality changes, but the impurity content increases with decreasing T_D.

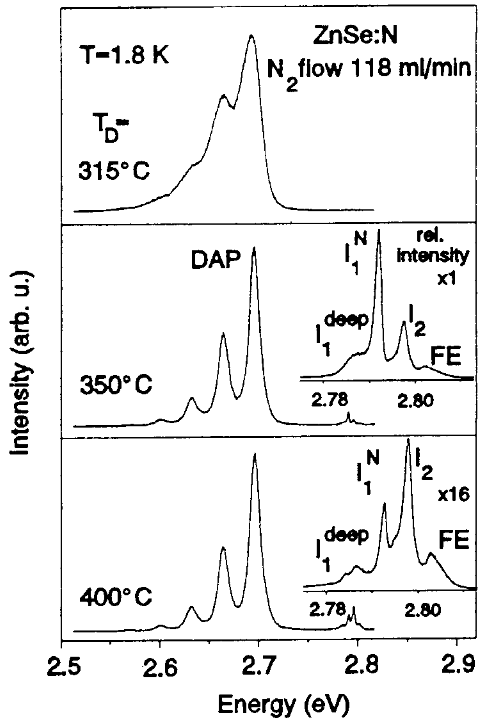

fig. 1
PL spectra (1.8 K) of homogeneously doped ZnSe:N grown at different temperatures.

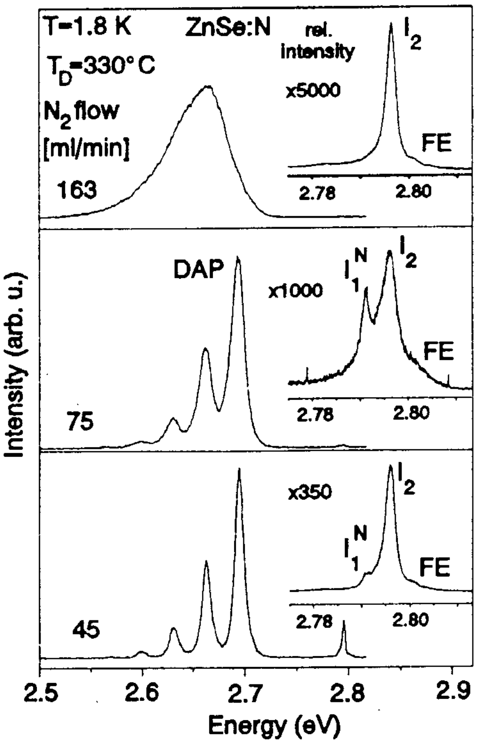

fig. 2
PL spectra (1.8 K) of ZnSe:N grown with various N_2 flows.

The spectra are dominated by donor bound exciton emissions at 2.797 eV (I_2), probably caused by Cl introduced as contamination from the Se precursor. Below a growth temperature of 350°C the Cl content becomes sufficient to suppress the free exciton emission. At 300°C the incorporation of shallow acceptors becomes important leading to I_1 and DAP emissions. Additionally, complexes of shallow acceptors and deep centres lead to I_1^{deep} emission. The best optical results were obtained in the temperature range between 330 and 350°C. In electrical measurements a background electron concentration in the range of $1x10^{16}$ to $2x10^{17}$ cm^{-3} was found.

Figure 1 compares the luminescence of homogeneously doped ZnSe:N layers grown at temperatures between 315 and 400°C. The spectra are dominated by DAP recombinations and the ratio R_{DAP} of the DAP and the exciton emission increases with decreasing T_D. Simultaneously the ratio between the I_1^N and the I_2 emission (R_{Ex}) increases, showing the drastical improvement of nitrogen incorporation on Se sites with decreasing temperature. The parallel development of the I_1^{deep} line indicates that nitrogen participates in these defects. Below 330°C exciton emission is no longer observed and the DAP band broadens. At a deposition temperature of 330°C we varied the nitrogen flow between 34 and 207 sml/min. SIMS measurements showed an increased nitrogen concentration (up to $2x10^{18}$ cm^{-3}) of the layers with increasing flow. The PL spectra of some of these samples are shown in figure 2. Up to a N_2 flow of 118 sml/min the intensity ratio R_{Ex} increases in the PL-spectra. At higher N_2 flow the ratio R_{Ex} decrease. The ratio R_{DAP} increases with increased nitrogen flow. The DAP-emissions and their phonon replica smear out to a broad band. Similar spectra have been reported for highly nitrogen doped MBE ZnSe epilayers [9] indicating a high N- concentration in the MOVPE layers. No correlation between the weak deep-centre emissions and the nitrogen doping is observed. C-V measurements prove that most of the N-doped samples are still n-type or semiinsulating. For the lack of p-conductivity there are a lot of different reasons. First the spectra and the C-V results of undoped samples show a contamination with donors which becomes more pronounced at lower growth temperatures. Thus, the samples are strongly n-type offering a high barrier for p-conductivity. Also, SIMS measurements show a hydrogen concentration up to $5x10^{18}$ cm^{-3} in the layers leading to a passivation of the N acceptor. However, samples grown under optimum conditions show pronounced I_1^N emission indicating the presence of unpassivated N-acceptors. Third, nitrogen is known to form donor-type defects at high N- concentrations in ZnSe [10] and there are hints for similar defects at low nitrogen concentrations. The PL spectra of N doped MOVPE samples presented in figure 1 and 2 indicate the formation of N related donors to be important at much lower N concentrations than in MBE. Reactions between the MO precursors and the activated N_2 stimulate the incorporation of hydrogen and the formation of nitrogen related donors. In order to prevent these effects the planar doping scheme was invented. Figure 3 compares the PL of samples grown under the same conditions but using different switching sequences as indicated. For homogeneous doping the high nitrogen flow leads to the broad DAP band and the lack of the I_1^N emissions. Using planar doping under the same growth conditions result in sharp DAP and dominating I_1^N emissions. Additional SIMS shows a reduced hydrogen concentration of $6x10^{17}$ cm^{-3}. However, the broader DAP spectrum demonstrate the more efficient doping under Zn-rich conditions. This is in accordance with similar experiments using MBE technique [8]. C-V measurements of a ZnSe:N layer grown at 330°C using Se-rich planar doping can be explained in terms of p-type conduction with N_A-N_D=$5x10^{17}$ cm^{-3} close to the Schottky contact decreasing to $3x10^{15}$ cm^{-3} at the ZnSe/GaAs interface. The transient of the I_1^N emission in time resolved PL of this layer is well fitted by a two-exponential decay. The luminescence rises faster than our experimental resolution of about 10 ps. The occurance of two different time constants is attributed to the inhomogeneity of the layer. The lifetime of the I_1^N emission line is a sensitive measure for the layer quality. Though it is still shorter than values observed for I_1 complexes in ZnSe bulk material [11] or MBE-ZnSe:N layers [12], it is longer than observed in homogeneously doped MOVPE ZnSe layers, indicating a superior sample quality obtained by planar doping. The decay of the DAP recombination can be used to evaluate the acceptor concentration. A good fit is obtained for N_A=$2.4x10^{17}$ cm^{-3} and a W_{max} of $3x10^7$ Hz. The acceptor concentration is in reasonable agreement with results of C-V and SIMS measurements and the low W_{max} indicates a low deep defect background.

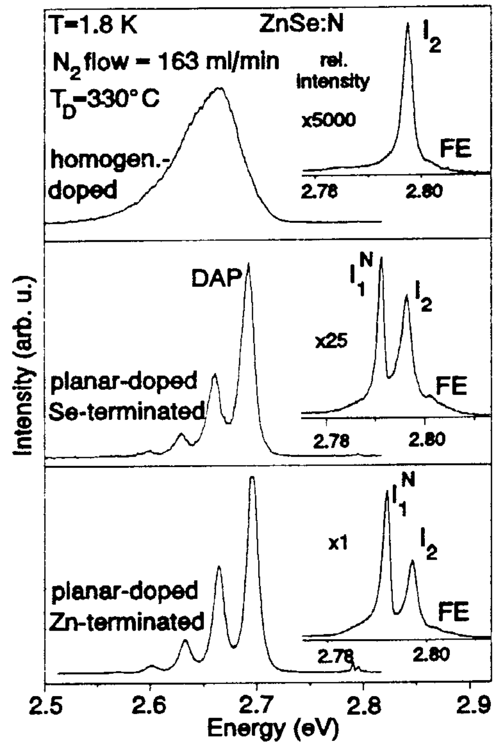

fig. 3
PL spectra of ZnSe:N grown with different doping schemes, but identical growth parameters.

IV) CONCLUSION

Undoped and nitrogen doped ZnSe epilayers grown by MOVPE using the precursor combination DTBSe/DMZn(TEN) have been demonstrated to possess excellent optical quality. Time resolved luminescence proves a low deep level defect background. Employing a N_2 plasma nitrogen concentrations up to $2x10^{18}$ cm^{-3} are obtained controlable by the N_2 flow or the growth temperature. Planar doping has been found to be a useful technique to avoid reactions responsible for the hydrogen incorporation and N-related donor formations. However, Cl contaminations of the used Se precursor still prevents reproducible p-type conductivity.

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