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Gallium and nitrogen ion implantation in MOVPE-grown ZnSe/GaAs

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We report on n- and p-type doping of MOVPE-grown ZnSe layers on GaAs substrates by implantation with gallium or nitrogen and subsequent annealing. The samples were analyzed by Hall measurements, photoluminescence, Raman scattering and far-infrared reflectivity. For Ga implantation a free-carrier concentration in ZnSe of about $n = 10^{17}$ cm^{-3} is achieved. Furthermore, we observe that the annealing procedure leads to a considerable diffusion of Zn across the epilayer–substrate interface into the GaAs substrate, resulting in a highly p-type layer of about 1 μm thickness. This interface layer complicates the analysis of p-type ZnSe layers. However, nitrogen incorporation is evident from SIMS measurements and PL spectra.

1. Introduction

ZnSe is a very suitable material for optoelectronic devices such as blue LED and laser diodes in the wavelength range below 450 nm [1]. The close matching of the lattice constants of ZnSe and GaAs allows the growth of nearly perfect epitaxial layers [2]. The growth of high-quality epitaxial layers of ZnSe and ZnSe-based ternary layers resulted in a pulsed blue laser, operating at 77 K [3]. A crucial aspect for optoelectronic applications is the achievement of controlled n- and p-type doping levels. Ion implantation is a fast and simple doping technology widely used for silicon and GaAs devices and integrated circuits. One of the most promising applications in ZnSe based optoelectronic devices would be a very thin but highly n- or p-type doped contact layer to improve the ohmic contacts which are still a limiting factor in blue lasers [3]. Recently, ZnSe and ZnS implantation experiments with lithium and sodium [4,5] as well as electroluminescence from a ZnSe p–n junction fabricated by nitrogen implantation [6] were reported. However, a detailed investigation of the dependence of electrical and optical properties on annealing and implantation parameters is still missing. Therefore, in this paper we present a study of the feasibility of n- or p-doping of ZnSe by the implantation of gallium or nitrogen. Optical and electrical experiments were used to determine the achieved doping level, the crystalline quality and the effects on the interface between the epitaxial layer and the substrate.

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2. Experimental

2.1. Sample preparation

The unintentionally doped ZnSe layers were grown on GaAs (1 0 0) substrates by atmospheric pressure MOVPE. We used DESe and DEZn as precursors and obtained n-type background carrier concentrations of about 10^{16} cm^{-3}. From photoluminescence measurements at 10 K, we can resolve free and bound excitons. The properties of the undoped layers were analyzed in detail recently [7]. The samples investigated in this paper were 4 μm thick. To achieve n- and p-type conductivity, the samples were implanted with gallium or nitrogen ions with doses of 2×10^{13} cm^{-2} and implantation energies up to 340 keV. A subsequent annealing is used to reconstruct the lattice distortions caused by the implantation process. The samples were covered with SiO_2 in order to prevent outdiffusion of Zn and Se during annealing. For transport measurements on n-type samples, indium ohmic contacts were alloyed at 350°C under a N_2/HCl atmosphere. Ohmic contacts to p-type samples were realized by the evaporation of 5 nm of chromium and 100 nm of gold.

2.2. Analysis

The optical analysis was performed by photoluminescence (PL), Raman spectroscopy and far-infrared reflectivity (FIR) experiments. Photoluminescence was excited by the 325 nm radiation of a He–Cd laser and analyzed using a 1 m SPEX monochromator giving a spectral resolution better than 0.03 nm. For the Raman analysis, we used an Ar-ion laser. The laser lines were varied between 514 nm and 457 nm, leading to a considerable variation of the penetration depth and the scattering efficiency in ZnSe. Spectra were taken in backscattering with polarization configuration $1\,0\,0$ $(0\,1\,0;\ 0\,0\,1)$ $\bar{1}\,0\,0$ at 300 and 77 K. The input power was 35 mW, while the focus diameter was about 0.1 mm. The scattered light was analyzed with a Spex 1402 double monochromator, using a RCA 14034A-02 GaAs photomultiplier for the detection. The spectral accuracy was ± 0.15 cm^{-1}. The FIR spectra were taken in the spectral region between 50 and 600 cm^{-1} at normal incidence, using a Bruker IFS 114 Fourier spectrometer and a bolometer detector. Standard van der Pauw Hall measurements were carried out at 300 and 77 K.

3. Results and discussion

3.1. Gallium implantation for n-type doping

SIMS measurements show that the peak gallium concentration is 10^{18} cm^{-3} and that the projected range of the ions in ZnSe is about 130 nm under the surface, which is almost the same as in GaAs because of the equal average mass. The PL spectra show donor–acceptor pair (DAP) recombinations at 2.73 and 2.75 eV. The near band edge emission intensity of these samples was a factor of two higher compared to the DAP emission while the intensity was comparable in samples annealed at 900°C for 20 s. The emission from donor bound excitons broadens compared to undoped samples. The Hall measurements for Ga-implanted samples yield n-type conductivity. The results at 300 K and 77 K are summarized in fig. 1. The sheet electron concentration versus annealing time are plotted with the annealing temperature as a parameter. We discuss the sheet carrier concentration since the gaussian implantation profile may change with the annealing conditions. As a general trend, we observed an increase in the carrier concentration with increasing annealing temperature and an-

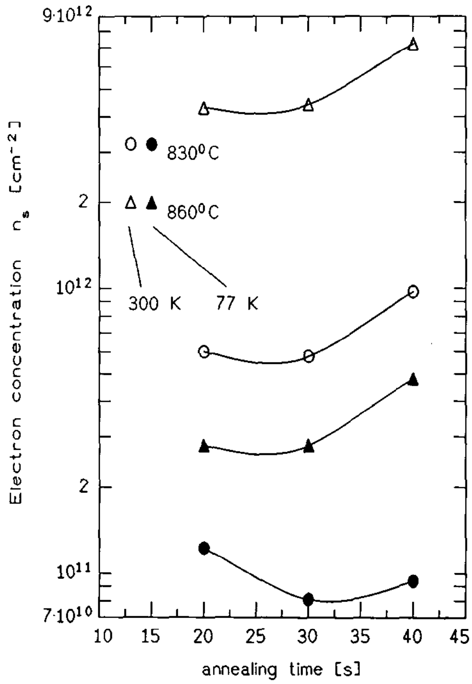

Fig. 1. Hall-determined electron concentration at 300 and 77 K for Ga-implanted ZnSe layers as a function of annealing time. The annealing temperatures were 830 and 860°C, respectively.

nealing time. At 77 K, all measured carrier concentrations were reduced due to carrier freeze out, but the general trend between 830 and 860°C annealed samples remained. The highest measured Hall mobility at 300 K was 300 $cm^2/V\,s$ for the sample annealed at 830°C for 20 s. Increasing the annealing time causes a decrease in the mobility of 240 $cm^2/V\,s$, consistent with the increase in the carrier concentration. At 77 K, the highest measured mobility is 800 $cm^2/V\,s$. The samples annealed at 860°C follow the same trend but the highest 300 K mobility is only 270 cm^2/Vs, and at 77 K the mobility increase is less pronounced ($\mu_{77} = 330\ cm^2/V\,s$).

The results of FIR reflectivity experiments for the analysis of free carriers are shown in fig. 2. To separate the effects of annealing and implantation, we compare an as-grown layer, a nonimplanted layer, annealed at 870°C for 30 s, and a Ga-implanted layer, annealed with the same parameters. The main structures in the spectra originate from the phonon-derived Restrahlenbande of ZnSe and GaAs. The free carrier (FC) concentration can be determined from an increase of the reflectance in the low frequency region due to screening of the electric field of the light. Obviously, already the annealing of a non-implanted sample induces major changes in the spectrum. We fitted the experimental spectra according to the Drude model, based on the superposition of harmonic oscillators. The best fit of spectrum (b) was obtained when assuming a heavily doped layer in the GaAs substrate. We interpret this layer as a result of Zn-diffusion across the interface, resulting in p-doping of the upper substrate region. Our fit yields a doping level of a few $10^{19}\ cm^{-3}$ and a thickness of 1.2 μm. This considerable diffusion is in agreement with the experimentally observed high diffusion coefficients of Zn in GaAs [8]. In our samples, the diffusion may be enhanced by the dislocations. The additional free electrons in ZnSe due to implantation (see sample (c)) cause minor changes in the FIR spectrum, which, however, cannot be evaluated quantitatively due to the dominating structure of the doped interface layer. However, we could optically detect the free electrons due to Ga implantation by Raman spectroscopy. Here the implantation leads to a shift of the LO phonon frequency of ZnSe. This shift arises from the coupling between the LO phonon and the free carriers [9]. We observe shifts up to 4.4 cm^{-1}, corresponding to a doping level of $n = 9.1 \times 10^{16}\ cm^{-3}$. To check the crystalline quality of the layers after implantation or annealing, we evaluated the spectral half width of the LO phonon and the intensity ratio of the forbidden TO to the allowed LO phonon in the Raman spectra. For an increased sensitivity, the samples were cooled to 77 K. Nonimplanted annealed samples show a slightly increased half width (4.5 cm^{-1}) with respect to as-grown samples (4 cm^{-1}), which is attributed to thermally induced defects. For implanted samples, we obtained half widths of 5 cm^{-1} and beyond, which is at least partly caused by the presence of free carriers. The same trend applies for the TO/LO intensity ratio, which is below 0.05 for the as-grown samples, 0.3 for the nonimplanted annealed samples and 0.4 for the implanted samples. Thus, the implantation induced defects do not completely vanish. In addition to the phonon peaks, a broad structure occurs in the Raman spectra of all annealed samples, centered at

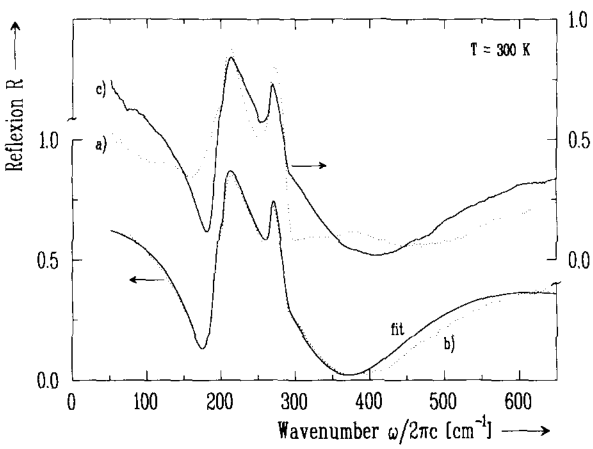

Fig. 2. Far-infrared reflectivity spectra of ZnSe/GaAs heterostructures at 300 K: (a) as-grown sample; (b) after annealing at 870°C for 30 s without implantation, the fitted curve is included as a solid line; (c) after implantation of gallium ($2 \times 10^{13}\ cm^{-2}$, 240 keV) and subsequent annealing at 870°C for 30 s.

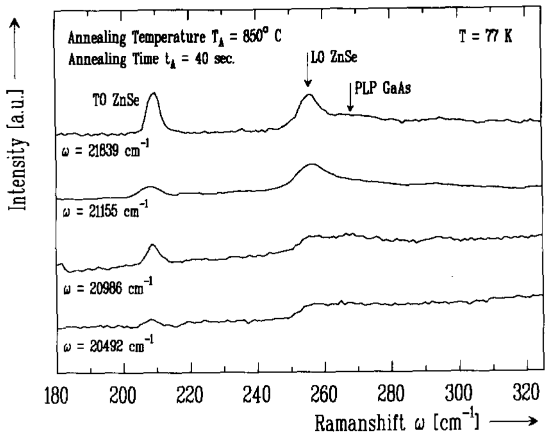

Fig. 3. Raman spectra of Ga-implanted ZnSe/GaAs heterostructures, taken at 77 K with different laser lines between 21 839 and 20 492 cm^{-1}.

about 265 cm^{-1}. To decide whether it originates from the ZnSe layer or from the GaAs substrate, we investigated its resonance behaviour for different laser lines. Figure 3 shows the results for laser lines between 20 492 and 21 839 cm^{-1}. The intensity of the 265 cm^{-1} structure is clearly coupled to the GaAs phonon intensity. We therefore interpret it as a coupled plasmon–LO-phonon (PLP) mode of GaAs, arising from the heavily doped interface region, in accordance with our FIR results.

3.2. Nitrogen implantation for p-type conductivity

To obtain p-type ZnSe, the as-grown layers were implanted with 2×10^{13} cm^{-2} nitrogen at 240 keV ion energy. After deposition of 150 nm SiO_2, they were annealed either at moderate temperatures (around 470°C) for some minutes or at high temperature (850°C) for some seconds. SIMS measurements show that the maximum of the implantation profile is 5×10^{17} cm^{-3} located at the surface after annealing. The concentration decreases down to 3×10^{16} cm^{-3} at 1 μm depth. Figure 4 shows the PL spectra of samples annealed at temperatures beyond 800°C, for 20–40 s, while those annealed for 5 min at 450–490°C are shown in fig. 5. The broad structures in the range down to 2 eV originate from

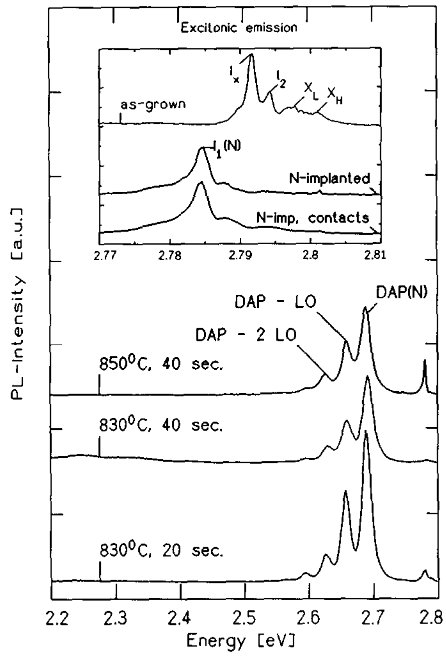

Fig. 4. 10 K photoluminescence spectra of N-implanted ZnSe layers, annealed between 20 and 40 s at temperatures beyond 800°C.

deep center (self-activated) luminescence. The superimposed fine structure is due to interference in the ZnSe layer. The photoluminescence spectra in fig. 5 show that for moderate temperature annealing, best results are achieved at 470°C. At this temperature, the ratio of donor–acceptor pair recombinations (DAP(N)) to deep centres (SA) is maximum. The highest peak at 2.695 eV can be associated with nitrogen [10]. The distance to the left-hand peaks (multiples of 31 meV) suggests the association with LO phonon replica. Comparison of the layers annealed at 470 and 490°C indicates that the characteristics of the donor–acceptor pair regions are similar. The high-temperature annealed samples in fig. 4 show very weak emission from self-activated (SA) centers that allows the conclusion that the crystalline quality is sufficiently high after annealing. The I_1 emission at 2.793 eV shown in the inset of fig. 4 can be attributed to an exciton bound to nitrogen [10]. The activation energy follows to be about 110 meV. The DA peak at 2.695 eV (460 nm) can be again associated with nitrogen and the left-

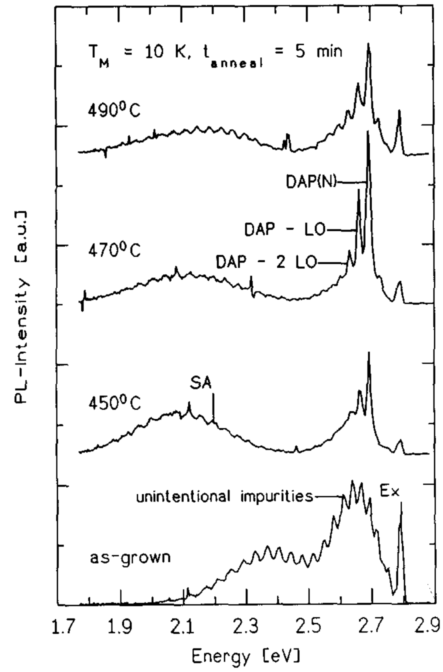

Fig. 5. 10 K photoluminescence spectra of N-implanted ZnSe layers, annealed for 5 min at various temperatures between 450 and 490°C.

hand peaks with LO-phonon replica [10]. Comparison of figs. 4 and 5 shows the superiority of the high-temperature annealing, because the ratio of DAP to SA is higher. Typical Hall mobilities of 70 $cm^2/V\,s$ at 300 K and 95 $cm^2/V\,s$ at 77 K ($p = 10^{17}$ cm^{-3}) were measured in nearly all samples independent of technological parameters. This is consistent with the presence of a highly p-conducting GaAs/Zn layer between substrate and epilayer, discussed in detail in the previous section.

4. Summary

We have shown that n-type conductivity of ZnSe can be achieved by gallium implantation. However, the crystalline quality is slightly deteriorated by the implantation process: the radiation damage cannot be reconstructed completely. In addition, the annealing induces a considerable diffusion of Zn into the GaAs substrate, resulting in a heavily doped layer (up to $p = 10^{19}$ cm^{-3}, $d = 1.2$ μm) at the interface. The implantation of nitrogen seems to yield p-type conduction. No unambiguous evidence of p-type conduction in ZnSe was obtained by Hall or FIR measurements since the p-ZnSe doping may be masked by the highly p-type conducting interface layer. Nitrogen incorporation into ZnSe can be concluded from the SIMS and PL measurements.

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