

## Development and characterization of II-VI blue-green diode lasers

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In this paper, we report the growth and characterization of II-VI devices grown by molecular beam epitaxy (MBE). The n-type doped ZnSe epilayers were obtained using iodine from an electrochemical cell and nitrogen from a RF plasma source was used for p-type doping. Capacitance-voltage ( $C-V$ ) electrochemical profiling of layers and devices has been used to ensure uniform n-type and p-type doping. The nitrogen doped epilayers show a compensation process which leads to the suggestion of a new deep donor which is a complex, such as the ( $V_{Se}-Zn-N_{Se}$ ) single donor which involves native Se vacancies. The fabrication of pn laser diodes and ZnSe/Zn<sub>0.82</sub>Cd<sub>0.18</sub>Se quantum well (QW) laser diodes is reported. The pn junctions show blue laser emission between 448-473 nm under pulsed current conditions at 4.2 K and the QW laser diode shows an excellent mode structure and emits at 474.8 nm at 77 K in pulsed mode operation.

### 1. Introduction

For three decades, the importance of II-VI semiconductor materials for making devices which emit in the blue-green wavelength region (ZnSe,  $E_g = 2.67$  eV at room temperature) has been known but research to produce such devices has been without success. A breakthrough was made in early 1991 when Haase et al. [1], at 3M Company Laboratories, demonstrated LEDs and blue-green semiconductor lasers and since then many other research groups [2,3,4] have produced similar laser structures. These important achievements were a consequence of successful p-type doping of ZnSe using an RF plasma nitrogen source from Oxford Applied Research [5,6]. High-quality n-type ZnSe had already been grown and so it was possible to

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### 2. Growth

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fabricate quantum well structures within pn junctions. Most of these laser diodes are based on quantum wells made of (Zn, Cd)Se with ZnSe or Zn(S, Se) as barriers but laser diodes with ZnSe as the emitting material are interesting because they will emit blue light at room temperature while (Zn, Cd)Se emission based material will emit blue-green light (around 500 nm) at room temperature. Okuyama et al [3], from Sony Corporation Research Center, have recently reported for the first time the fabrication of a ZnSe/(Zn, Mg)(S, Se) laser diode operating at 77 K and blue stimulated emission was observed at 447 nm.

An important problem in developing II-VI laser devices is the making of good ohmic contacts to the p-type ZnSe and related alloys. This difficulty arises because of the depth of the valence band [7] of ZnSe which is approximately -6.7 eV with respect to the vacuum level. Most metals therefore form 'classical' Schottky barriers on ZnSe and other wide bandgap materials so that high voltages are needed to drive current through the devices (10-25 volt or more).

beam epitaxy (MBE). The nitrogen from a RF plasma layers and devices has been a sation process which leads or which involves native Se ser diodes is reported. The at 4.2 K and the QW laser ation.

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2. Growth

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summary of II-VI work carried ratory and includes the dem- and quantum well laser diodes. um confined Stark effect also been made but are dis- 8].

structures were fabricated by itaxy (MBE) using a Vacuum growth system. GaAs sub- ally cleaned and the ZnSe and were grown at 280°C using dsen cell sources of zinc, nium. The substrate tempera- ed by an infrared optical ur structures so far, no GaAs been grown on the GaAs sed by Haase et al. [1] in the first II-VI laser diodes.

MBE growth of ZnSe, n-type rier concentrations up to n obtained with gallium [9] as , more recently n-type doping rier concentrations levels been achieved [10,11] using Cl<sub>2</sub> and it is now widely used in t. Iodine had also been used CVD using ethyl iodide and and in metal organic MBE methyl iodide [13] as a source. o report the growth of n-type h carrier concentrations rang-  $10^{19}$  cm<sup>-3</sup>, using a solid state l as a source of iodine [14,15]. trations were measured using l variable temperature Hall in der Pauw configuration). ents showed a maximum /s at 200 K which is in good e MOCVD results. At room mobility is 280 cm<sup>2</sup>/V s. The are well-behaved n-type ma- by photoluminescence, Hall and the presence of a uniform on through the epilayer re-

flects the uniform doping flux from the electro- chemical cell. The advantage of the electrochem- ical iodine source is that the source material is not volatile and only small quantities of iodine are produced which leads to more accurate control of the doping levels. Another major benefit of the electrochemical cell is the ability to switch between doping levels with a time con- stant of less than one second and so we have used the iodine cell to grow both uniformly doped ZnSe and layers with different doping levels in the form of staircase structures [14].

There has been a long history of attempts to dope ZnSe p-type. Lithium has been used with doping levels up to  $10^{17}$  cm<sup>-3</sup> but the Li atoms in ZnSe are very mobile and there would be prob- lems with device stability. We have recently attempted to use potassium [16] from an electro- chemical cell but only low levels of doping were observed because of surface segregation of the potassium during growth. Park et al. [5] from the University of Florida and Ohkawa et al. [6] from Matsushita were the first to successfully dope MBE ZnSe using a nitrogen RF plasma source supplied by Oxford Applied Research. Doping levels up to  $10^{18}$  cm<sup>-3</sup> have been reported but the material is difficult to characterise because of poor ohmic contacts. Also, doping levels greater than  $5 \times 10^{17} - 1 \times 10^{18}$  cm<sup>-3</sup> are difficult to achieve since additional nitrogen is not electrical- ly active. Nitrogen creates an acceptor with a binding energy of 110 meV and by examining the photoluminescence (PL) spectra from ZnSe: N we have observed different donor acceptor pairs (DAP) for different nitrogen concentrations ( $N_A - N_D$ ). For low nitrogen concentrations the DAP recombination involves the 110 meV nitro- gen acceptor and the residual shallow donor with a binding energy of 26 meV giving an emission with no-phonon line at 2.696 eV and this band dominates the PL spectra. When the carrier concentration reaches approximately  $1 \times 10^{17}$  cm<sup>-3</sup> another broader DAP band is ob- served and it dominates the emission when ( $N_A - N_D$ ) is over approximately  $4 \times 10^{17}$  cm<sup>-3</sup>. This DAP emission has lower energy (2.678 eV) and corresponds to recombination involving the 110 meV nitrogen acceptor and a new deep donor

with a binding energy of 44 meV. This interpretation has been supported by temperature-dependent photoluminescence measurements that demonstrate that the two distinct DAP emissions are due to the presence of two donors. We have proposed that the new compensating donor is a complex involving a native defect such as the  $(V_{Se}-Zn-N_{Se})$  single donor [17].

Measurements also show that a depletion layer forms on the surface of the p-type layer [17]. No such changes in carrier concentration profiles have been observed in n-type material and so the observed change in p-type doping is believed to originate from the surface. This is consistent with the role of native defects in the compensation process and supports our proposed defect model for the deep donor since the surface is a source of  $V_{Se}$  which could diffuse to electrically active nitrogen acceptors. We have also carried out photoluminescence measurements on selected nitrogen doped ZnSe samples, measured a few days after growth and again six weeks later. By comparing these measurements we observe that the intensity of the deeper DAP band has increased relative to the shallow DAP band. Further evidence will be published later.

The illumination of the growth surface with above bandgap radiation during MBE growth is known to have several effects, including modulation of doping concentrations. A Kr ion laser (351 nm) was used as a UV source and we have shown, in the case of n-type iodine doping of ZnSe, that dopant incorporation is dramatically reduced, even at low levels of irradiation [18]. In the case of the p-type dopant, the incorporation and activation of nitrogen in ZnSe could be affected by above bandgap illumination during growth via a number of routes, which can be either primary effects on the nitrogen incorporation or activation, or secondary effects resulting from the modification of other growth processes. For instance, the incorporation rate could be altered directly by changes in surface potential affecting the nitrogen sticking coefficient, or the incorporation rate might also be affected indirectly by illumination effects on the matrix elements [19]. Our experiments show that in the case of laser assisted growth of nitrogen doped

ZnSe at 280°C, doping levels can be increased but these appear primarily due to changes in Se surface coverage due to the irradiation. We have found that Se coverage is reduced by above bandgap illumination for the p-type material as is the case with undoped and n-type material and so the laser induced increase in nitrogen incorporation is due to the change in the Zn:Se ratio caused by the UV radiation.

### 3. pn diode laser

The standard technique for obtaining carrier concentration profiles in semiconductors relies on capacitance-voltage (C-V) profiling. Electrochemical (C-V) profiling through the laser structures was carried out using a modified BIO-RAD PN 4300 profiler for both carrier concentration and bandgap photo-voltage measurements (PVS). Initially, these measurements were made using an ultrasonic probe to remove the Se deposit which appeared during the etching process using an 0.2M NaOH electrolyte [20] but more recently we have used an NaOH (1M):Na<sub>2</sub>SO<sub>3</sub> (1M) electrolyte which gives excellent results without the ultrasonic cleaning [21].

Figure 1 illustrates the first reported C-V profile of a ZnSe pn junction obtained using the BIO-RAD profiler [22]. The p-type and n-type layers which are approximately 1  $\mu$ m thick are clearly resolved and have doping levels  $4 \times 10^{17}$  and  $1 \times 10^{18}$  cm<sup>-3</sup>, respectively. The large spike at the interface between the p-type and n-type layer is an artefact of the C-V measurement technique. The pn junction lasers were fabricated with an 0.2 mm gold stripe on the top of the p-type layer of the diode. The samples were then cleaved to a length of about 1 mm and a rear ohmic contact was made with indium onto the n<sup>+</sup> GaAs substrate. The diodes emitted in forward bias with either CW or pulsed excitation from room temperature down to helium temperature. All the spectra were obtained using a 0.85 m SPEX double monochromator and a Stanford gated photon counter. Electroluminescence for low current injection is due to pair

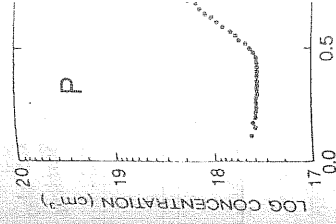


Fig. 1. Electrochemical junction giving  $(N_A - N_D)$  in the n region.

recombination in the since in these diodes much greater than the inter-impurity type region has the photoluminescence p-type layer is identical and corresponding al. [23] in highly dc self-compensation at emission at a very blue emission increased and at 4.2. ture. At 4.2 K a structure was obtained und below threshold. width half-maximum the current is increased emission appears spectrum distributed dominant emission mately 458 nm and the conduction be donor-to-acceptor (rent threshold for around 100 mA which In some devices, observed up to 4 exciton related rec



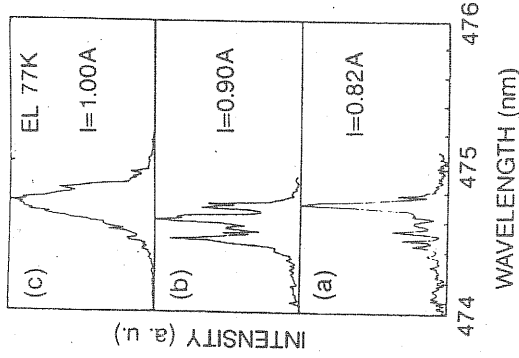


Fig. 2. Emission spectra at 77 K for a (Zn, Cd)Se/ZnSe MQW laser diode at three different injection current levels: (a) 0.82 A, (b) 0.90 A and (c) 1.0 A.

above the threshold, one longitudinal mode dominated and the device operated in the fundamental lateral mode. With increasing current, a typical multimode spectrum was observed and the longitudinal mode spacing was 0.026 nm corresponding to that expected for a 920  $\mu\text{m}$  cavity length.

## 5. Conclusion

In conclusion, we have fabricated Zn(Cd, Se)/ZnSe quantum well laser diodes on GaAs substrates without using epitaxial GaAs layers. We have used electrochemical C-V profiling to confirm uniform carrier concentration throughout these structures. We have also shown that an electrochemical source of iodine can be used to grow well-behaved n-type ZnSe with doping levels up to  $10^{19} \text{ cm}^{-3}$ .

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