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Blue and Green Laser Diodes and LEDs in ZnSe-Based Quantum Structures

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Recent advances in pn-junction quantum well light emitter structures in the blue-green in the authors laboratories are reviewed. The results include relatively efficient (0.1% at T=300 K) LEDs and injection diode lasers, the latter having reached cw operation at T=77K and pulsed to room temperature with threshold current density of 1 kA/cm².

A major milestone in the field of wide bandgap optoelectronic devices was reached in 1991, when two research groups working independently achieved the proof-of-concept demonstration of a blue-green diode laser in ZnSe-based heterostructures [1],[2]. This followed a three decade long search for a semiconductor laser at short visible wavelengths. Todate, both groups, one at 3M Corporate Research Laboratories and our Brown-Purdue team have demonstrated continuous-wave operation at T = 77K in the wavelength regime of 470-480 nm, while pulsed room temperature operation has been observed at somewhat longer wavelengths (500-510 nm) [3], [13]. As a natural byproduct of this device and materials science research, light emitting diodes (LEDs) of potential technological significance have also been fabricated. In this presentation, we review some of the pertinent results in our laboratories, including both LEDs and diode lasers.

Much of the recent progress ows its origin to the application of modern epitaxial methods, especially MBE, to the synthesis of wide gap II-VI semiconductors and the parallel realization of optoelectronically useful heterostructures. It is also important to acknowlege another seminal factor towards the recent breakthrough of the diode laser, namely the progress in p-type doping of ZnSe, chiefly by Park et al [4] and Ohkawa et al [5]. In terms of the heterostructure details, the choice for the optically and electronically active region in the new light emitting devices has so far chiefly been the (Zn,Cd)Se/ZnSe or (Zn,Cd)Se/Zn(S,Se) quantum well (QW), a configuration which had been shown through earlier optical pumping studies to be a prime candidate for laser devices within II-VI heterostructures [6]. Electronic confinement (type I quantum well) is quite robust in this system, unlike that encountered with many other wide gap II-VI heterostructures. As a consequence, the quasi-2 dimensional aspect of this system also manifests itself in strong excitonic effects which further enhance the interband optical cross-sections, observed to room temperature and beyond [7].

Figure 1 shows the schematics of some of the principal p-n heterojunction configurations used by the authors in the fabrication of LEDs and diode lasers. The benefit of a III-V buffer layer in the MBE growth of such structures is a high quality heterovalent electronic interface, as well as lattice matching of the II-VI superstructure with the buffer/substrate. In such a way we have built devices on structures where only the (Zn,Cd)Se QW layers are strained and remain in the pseudomorphic regime so that the strain



induced misfit dislocation density remains below 10^5 cm⁻² [8]. An illustration of the uniform electronic quality of the III-V/II-VI interface is shown in the upper trace of Figure 2 which depicts light emission from a spatially patterned LED structure [9]. While the electrical contact to the top n⁺-ZnSe layer is only applied locally, blue/green emission extends quite uniformly over the entire lithographically defined surface area. The bottom portion shows a seven segment LED where an ITO transparent top layer has been applied [10]. Figure 3 shows the emission characteristics from an LED at room temperature, operating at $\lambda = 494$ nm [8]. For this device, we measured a differential quantum efficiency of nearly 0.1%. The isoelectronic planar doping [11] of such a structure with Te readily leads to bright green LEDs at wavelengths in the range of 530-550 nm.

Photographic image of the laser emission is shown in Figure 4 where the multiple transverse modes of this relatively wide (20 μ m) stripe-geometry mesa device are seen. Grating surface emitting structures have been realized in optically pumped structures [12]. An illustration of the diode laser performance is given in Figure 5 which shows the emission spectrum and output power for pulsed operation at room temperature [13]. In these particular (Zn,Cd)Se/Zn(S,Se) QW laser devices, the end facets were coated for reduction of the threshold current density to 1 kA/cm² (at T = 77K, we measured I_{th} = 220 A/cm²). Without the coated facets, heating due to higher currents makes the reaching of room temperature operation difficult and devices are only short lived; the output characteristics of such devices are shown in Figure 5 [3]. We also mention that in initial studies of the gain switching in our lasers, optical pulse generation on a sub-100 psec timescale has been accomplished.



Fig. 2. Lithographically defined LEDs; (top) demonstration of lateral current spreading, (bottom) numeric display.

An important requirement for further improvement of the laser devices towards eventual room temperature, cw operation, is the improvement of electrical contacts in the pn-junction devices. The range of present issues and challenges are both fundamental and practical, both intrinsic and extrinsic to the materials and structures employed. Intrinsic aspects are a natural part of the landscape for any wide gap semiconductor



Fig. 3: Output characteristics of a MQW LED structure at room temperature

when considering ohmic contact to common metals. The problem is asymmetric at present with the ZnSe-based device structures in that maximum levels of p-doping ($\approx 10^{18}$ cm⁻³ with nitrogen as the dopant) are considerably lower than those for n-doping ($\approx 10^{19}$ cm⁻³ with Chlorine); hence Schottky-like barriers are particularly pronounced in the former case. Attempts to ameliorate the situation with low temperature MBE growth of p-ZnSe contact layers appears to have had some success, though voltages of 15-25 V are still required for diode laser action.

A similar problem of barrier resistance occurs at the II-VI/III-V heterointerface for p-type materials. Again, an effectively reverse bias (GaAs/ZnSe) junction will appear in series with the forward biased ZnSe QW pn-junction and leads to substantial nonlinear impedances in the vertical transport. This configuration also calls for significant future device development. A number of heterojunction and

improvement in the p-doping levels with ZnSe for future device development. A number of heterojunction and superlattice "bandstructure engineering" schemes are presently pursued as an alternative for solutions of the contact problem.

Finally, device applications aside, these new II-VI quantum well based structures offer an excellent



Fig.4: Photographic illustration of the blue-green diode laser output

opportunity for novel 2D exciton physics. In particular, by quantum confinement one can obtain the situation where the exciton binding energy exceeds that of the longitudinal phonon energy. Hence, the normally very strong Fröhlich interaction induced exciton dissociation into free electronhole pair states at elevated temperatures (in the relatively ionic II-VI's) is much reduced. Given also the robustness of the exciton gas against a phase transition into an electronhole plasma, it follows that quasi-2D excitons can participate in the formation of gain and laser emission. Three points of evidence indicate that the n=1 HH exciton state in the (Zn,Cd)Se/ZnSe and (Zn,Cd)Se/Zn(S,Se) QW is directly responsible for laser action at T=77 K, and is likely to be very important up to room temperature [14]. These are (i) close spectral correlation between exciton absorption and

stimulated emission, (ii) achieving of laser action under

direct resonant (optical) pumping into the exciton ground state, and (iii) the measurement of gain in the presence of a partially saturated but still-present exciton absorption resonance (see Figure 6). These results are drawn together into a model in which the exciton gain is realized by a combination of phase-space filling and exciton relaxation kinetics.

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Emission Intensity (arb.units) T=295K | > | _{th} l < l _{th} 2.40 2.45 2.50 2.55 Photon Energy (eV) (Zn,Cd)Se/Zn(S,Se) MQW 15 T= 295 K Output Power (mW) 10 5 0 500 1000 1500 2000 Current Density (A/cm²)

Fig. 5: Output characteristics of ZnCdSe/ZnSSe diode laser at room temperature (pulsed)

Fig. 6: Time-resolved excite-probe spectroscopy at the n=1 HH exciton resonance of a (Zn,Cd)Se MQW. Following femtosecond short pulse excitation, the diffrential probe transmission ($\Delta T/T$) shows real gain developing on the low energy side of the exciton resonance in a few psec. Laser spectrum can be measured in edge emission and coincides with the exciton gain regime (inset).