

The pseudomorphic structure used in a quaternary ZnMgSSe-based injection laser. A ZnCdSe quantum well (QW) active layer with ZnSSe guiding layers for optical confinement is clad with ZnMgSSe layers having negligible lattice mismatch with the GaAs substrate. Contact to the nitrogen-doped p-type ZnSe layer is made via a ZnSe-ZnTe digitally alloyed layer.

BLUE-GREEN SEMICONDUCTOR LASERS

Progressing Towards Viable ZnSe Lasers

Diego Olego of the Philips Laboratories, Briarcliff Manor, NY, USA, reports that steady progress continues to characterize the development of the all-important ZnSe-based short-wavelength semiconductor laser.

Major potential commercial applications, including those in high-density optical recording, displays, sensing, printing, and medicine, are generating considerable interest in short-wavelength solid-state light emitters. So it is not surprising that the development of semiconductor laser diodes emitting in the blue and green spectral regions is attracting considerable attention. Two direct band gap semiconductor systems — one based on the so-called wide band gap II-VI compounds, the other on the III-V compounds — are well suited for generating green and blue light (ZnSe and GaN are typical representatives of each system, respectively).

Research prototypes of ZnSe-based lasers have been demonstrated, and the performance of these devices, which so far operate mostly in the green and blue-green spectral regions, has improved continuously since the first laser demonstration. Very bright blue and green-blue GaN-based light emitting diodes (LED) are commercially available. However, the transition from spontaneous emission in LEDs to laser oscillations has not yet been achieved for GaN (a GaN-based laser could expand the laser wavelength frontier into the near-ultraviolet at wavelengths of about 400 nm or less). So in reviewing the latest results, as well as the remaining challenges, for the development and application of commercially viable short-wavelength solid-state devices, this article focuses on the ZnSe system.

The ZnCdSe Breakthrough

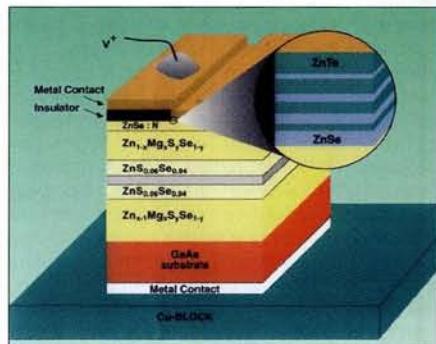
It was a group from the Photonics Laboratory of the 3M company that announced, in the summer of 1991 [1], the first demonstration of a ZnSe-based injection laser. This followed shortly after the breakthrough in obtaining p-type doping of ZnSe, which had remained elusive for decades [2]. This p-type conductivity was achieved by incorporating nitrogen acceptors (delivered from a plasma source generating free

radicals) during layer-by-layer growth by molecular-beam epitaxy (MBE) techniques.

The 3M device comprised a separate confinement heterostructure grown on a GaAs substrate. A strained $Zn_{1-x}Cd_xSe$ ($x \approx 0.2$) quantum well acted as the active region for light generation, and the quantum well was embedded in ZnSe layers, the so-called guiding region, for optical confinement of the light. Finally, the active and guiding layers were clad with ZnS_xSe_{1-x} ($x \approx 0.07$) layers to help the electrical injection of electrons and holes into the active layer. The laser demonstration by the 3M company came at a time when the robustness of wide band gap II-VI materials for stimulated emission by carrier injection in p-n junctions was being severely questioned.

In the 3M laser structure, the cladding ZnS_xSe_{1-x} layers are lattice matched to the GaAs substrate. On the other hand, there is a sizable lattice mismatch of about 0.27% between ZnSe and ZnS_xSe_{1-x} . This mismatch gives rise to structural defects threading through the active region with area densities in excess of 10^8 cm^{-2} . To avoid these unwanted defects, most researchers now prefer a laser structure in which the quaternary alloy $Zn_{1-x}Mg_xS_ySe_{1-y}$ is used for cladding layers and ZnS_xSe_{1-x} replaces ZnSe in the guiding region. By carefully adjusting the composition of Mg and S (x and y in the neighbourhood of 0.10), the quaternary alloy can be lattice matched to both the GaAs substrate and the ZnS_xSe_{1-x} , thus eliminating lattice mismatch-related defects.

The figure illustrating the quaternary laser structure shows that a $Zn_{1-x}Cd_xSe$ quantum well has been retained as the active region. Typical band gap energies at room temperature of the alloys in the quaternary laser are 2.42, 2.72 and 2.84 eV for $Zn_{1-x}Cd_xS$, ZnS_xSe_{1-x} and $Zn_{1-x}Mg_xS_ySe_{1-y}$, respectively. An additional advantage of the quaternary laser is the improved carrier confinement and optical guiding owing to the larger band gap of $Zn_{1-x}Mg_xS_ySe_{1-y}$ when compared with ZnS_xSe_{1-x} . It should be noted in the figure that a layered heterojunction material (a so-called ZnTe-ZnSe digitally alloyed contact layer) which changes the composition gradually from ZnTe to ZnSe provides the upper contact to the p-type layer. Contact schemes based on semiconducting heterojunctions are necessary since unfavourable Schottky barrier heights preclude conventional ohmic metal contacts to p-type ZnSe.



Today's Quaternary ZnMgSSe System

Building upon the 3M laser structure, today's quaternary laser symbolizes the combined effort of the wide band gap II-VI research community. Sufficient critical mass has been reached to enable cross-fertilization between groups. After MBE growth of $Zn_{1-x}Mg_xS_ySe_{1-y}$ had been pioneered by Sony [3], the first separate confinement quaternary laser was grown at Philips [4], while the collaboration between Brown University and Purdue University (both in the USA) spearheaded the development of reliable ZnTe-ZnSe digital contacts [5].

With the $Zn_{1-x}Mg_xS_ySe_{1-y}$ quaternary laser, continuous wave (cw) operation in the green has been achieved up to 80°C and pulse operation up to 120°C. At the present time, two groups (SONY and the 3M-Philips joint programme) have obtained cw lifetimes in excess of one hour. Other noteworthy accomplishments at the device level are the demonstration of index-guided structures, threshold voltages of about 4 V, and a cw output well in excess of 30 mW at room temperature. Many of these figures-of-merit will certainly change in the near future given the rapid pace of progress.

Challenges

The main challenges facing the development of ZnSe-based lasers involve extending the lifetime of the laser device and reducing the emission wavelength into the blue. The lifetime is limited at this stage by the presence of grown-in stacking fault defects with typical area densities of between 10^5 and 10^6 defects per cm^2 (the stacking faults become the dominant defects once lattice mismatch induced defects have been suppressed). Originating at the interface between the substrate and the II-VI layers, they degrade the light output by generating additional defects which thread into the active region during laser operation. The stacking fault density has to be reduced by at least two orders of magnitude in order to extend the laser lifetime towards practical devices.

Two approaches are adopted in aiming to reduce the stacking fault density. They involve either the careful control of the GaAs surface and precise adjustment of the first stages of the growth of ZnSe layers on the GaAs (heteroepitaxy) or the growth of ZnSe layers on ZnSe substrates (homoepitaxy). The heteroepitaxy approach (ZnSe and GaAs) entails the use of in-situ grown GaAs

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Opening and Closing Families

buffer layers before ZnSe deposition. The scarcity of good quality ZnSe substrates severely limits the impact of the homoepitaxy route.

Related to the laser lifetime is the performance of the ZnTe-ZnSe heterojunction contacts. Although, these contacts do not limit the lifetime of today's research lasers, they will have to further improve if they are to satisfy the lifetime demands placed on commercial devices.

Decreasing the wavelength into the blue spectral region below 480 nm involves the elimination of Cd in the quantum well together with the growth and p-type doping of $Zn_{1-x}Mg_xS_ySe_{1-y}$ having a band gap greater than 3 eV (x and y around 0.20). Some studies have shown that the doping efficiency drastically reduces as the band gap increases above this value. So further research is needed to ascertain if this reduction is intrinsic to the material or if it is affected by the present state-of-the-art in MBE growth technology. The smallest wavelength achieved so far with a ZnSe-based laser is 468 nm [6].

Since the demonstration of the first ZnSe laser, MBE has remained the growth technology of choice. Metalorganic chemical vapour deposition (MOCVD), the other commonly used epitaxial technology for optoelectronic devices, has failed so far to deliver reproducible p-type doping of ZnSe. The problem is that nitrogen acceptors are passivated by hydrogen atoms, the unwanted by-products of the conventional MOCVD process. Alternative chemical sources for the growth by MOCVD of ZnSe are being actively sought in order to overcome passivation by hydrogen.

One can conclude that steady progress has characterized the development of the ZnSe semiconductor laser. Many elements of the road map towards a reliable technology have been identified. Some of them are of a fundamental nature, such as the doping of wide band gap semiconductors to obtain laser devices that emit in the blue. Others, such as the role of defects in degrading the light output, recall similar challenges confronted in the past while developing today's conventional GaAs and InP lasers. It is expected that with improved contacts, further reductions in defect density, and refinements in device processing, the cw lifetime and other performance parameters of ZnSe lasers will keep evolving towards commercially acceptable levels.

[1] Haase M.A. et al., *Appl. Phys. Lett.* **59** (1991) 1273.

[2] Park R.M. et al., *Appl. Phys. Lett.* **57** (1990) 2127; Ohkawa K. et al., *Japan. J. Appl. Phys.* **30** (1991) L152.

[3] Okuyama H., *J. Cryst. Growth* **117** (1992) 139.

[4] Gaines J. et al., *Appl. Phys. Lett.* **62** (1993) 2462.

[5] Fan Y. et al., *Appl. Phys. Lett.* **61** (1992) 3160.

[6] Grillo D. et al., *Electronics Lett.* **30** (1994) 2131.

The 1995 Nobel Prize in Physics has been awarded to **Martin L. Perl**, Stanford University, CA, USA, for the discovery of the tau lepton and to **Frederick Reines**, University of California-Irvine, CA, USA, for the detection of the neutrino.

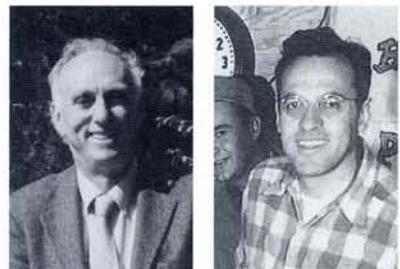
In today's language, the discovery of the neutrino closed the first family of quarks and leptons whereas the discovery of the tau lepton opened unexpectedly the third family of fundamental particles (which was closed recently with the discovery of the top quark).

The discovery of the tau takes us back 20 years back to the Stanford Linear Accelerator Center (SLAC), where the 80 m in diameter electron-positron collider ring SPEAR (see figure) was opening up a new range of energy - enough, as it turned out, to produce a tau together with its antiparticle. The tau is about 3500 times heavier than the electron, its cousin in the first family, and about 1.7 times heavier than the muon, its cousin in the second family. Each charged lepton is associated with a specific neutrino, which is massless at the precision of present-day measurements. CERN's Large Electron-Positron collider has confirmed the existence of three, and only three, neutrinos and the three related families represent the building blocks of Nature as we know it today.

The discovery of the tau was not an easy matter. There was no idea at the time whether such a particle existed and, of course, nothing was known about the most promising mass range to probe. Previous searches for a new lepton (why not one more since the muon was there together with the electron ?) had been negative. One could simply search with determination, an open mind and a liking for the unexpected — qualities which Martin Perl exemplified.

The signature of the tau is offered by the production of a tau-antitau pair in electron-positron annihilation. The tau may decay into an electron together with its antineutrino and a tau neutrino, while the antitau can give an antimuon together with its neutrino and a tau neutrino. The simultaneous appearance of an electron and an antimuon signals something *a priori* very special. The neutrinos are, however, undetectable and only the overall energy balance shows an apparent deficiency which is associated with their presence. The signature is thus clear, but hard to establish with certainty. After the first announcement, it still took a great experimental effort by the SLAC team to generate convincing evidence for the existence of the tau.

The tau not only heralded the appearance of the third family with its b and t quarks but also became a very powerful tool in particle physics. Its production and decay (an analyzer of its polarization) provide, in particular, precious information about spin effects.



M.L. Perl (left) in 1987 and F. Reines in 1953.

With the discovery of the neutrino we go back 40 years. The neutrino had been postulated by Pauli in 1930 in order to solve the problem of energy conservation in β -decay. It was shortly after incorporated by Fermi in his theory of β -decay. There was very soon no doubt that the neutrino existed, but it was realized that the low-energy neutrinos of β -decay had mean-free paths in matter that were measured in light years! So the neutrino seemed to be unobservable. But, as Pauli said in 1956: "*The extraordinary technical difficulties of the experimental demonstration of this reaction (the capture of a neutrino) were finally overcome by Cowan and Reines*". Clyde L. Cowan has since died, and Reines is now acknowledged for a major experimental achievement.

The Reines-Cowan experiment used a very powerful nuclear reactor as an intense source of (anti)neutrinos. Their detector was a barrel filled with about half a cubic metre of water containing cadmium chloride and placed between liquid scintillation detectors (see figure). Neutrinos could thus be captured in an unambiguous way. The antineutrino hits a proton which turns into a neutron with the production of a positron. The positron annihilates against an electron with the production of specific γ -rays which are detected. The capture of the neutron in cadmium also yields γ -rays. Detected about a microsecond later, they give a delayed coincidence signal to provide the signature.

They were long struggles with a low signal and a large background. But the neutrino was finally identified as a *bona fide* particle and it has since become a very powerful tool in particle physics. Its mean free path in matter decreases strongly with energy so high-energy neutrinos, produced with an intense flux from an accelerator, have become very powerful probes for studying the quark structure of matter. Neutrino scattering experiments also provided the first experimental evidence for the electroweak theory of particle physics with the discovery of the "neutral current" interaction. Neutrinos allow us to "see" inside the sun and play prominent roles in flares from supernovae and in our description of the Big Bang. So they have much to do with the structure of the cosmos at large. There remain today fascinating questions associated with the neutrino mass and with possible transformations between the three different neutrino species.

M. Jacob, CERN, Geneva

