The International Conference on II-VI Compounds & Devices

August 13th-18th, Heriot-Watt University

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An atmosphere of anticipation resided at the opening session of this, the seventh international II-VI conference. Over the past two years since the last meeting at Newport, Rhode Island, the only headline news in the II-VI community was the slow but a relentless increase in the lifetimes of blue emitting laser diodes. Delegates attending the device sessions expected something spectacular, since all the major players, Sony, Phillips, 3M and Brown-Purdue had something to say. From very early on in the conference the message was clear; there are no shortcuts in the development of these devices. The problems hinted at four years ago, and highlighted two years ago, are still with us, the community just has a greater insight into them now. Overall, however, the underlying feel of this meeting was of diversification and expansion of the range of research undertaken in the II-VI field, along with a more concentrated effort on the problems specific to lasers and LEDs.

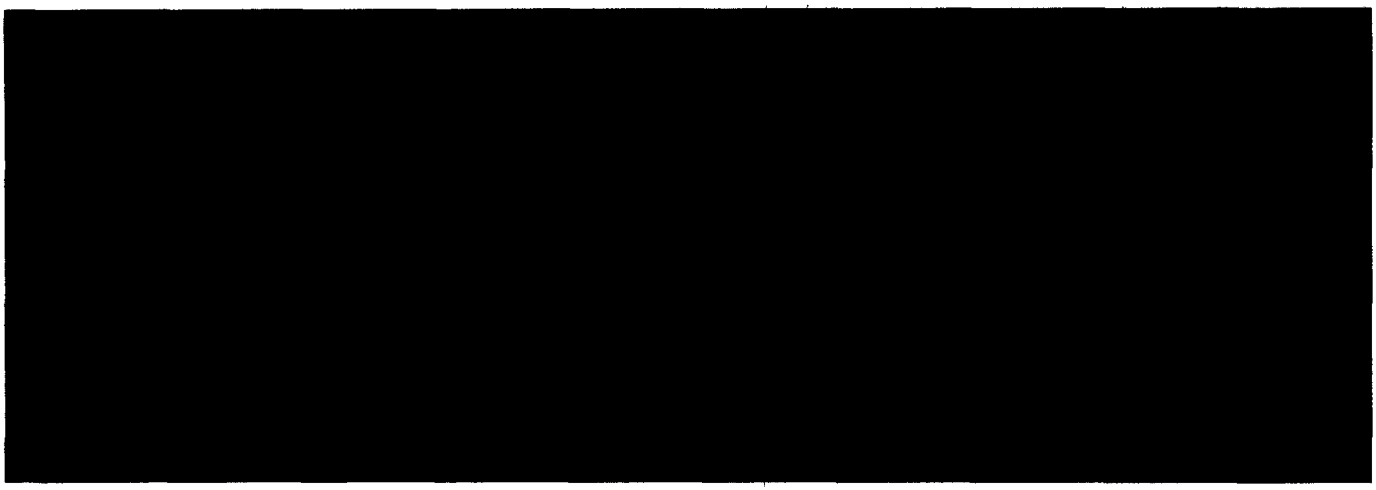
As at Newport, many of the invited papers were laser oriented, but the number of sessions devoted solely to blue laser development was reduced. The aim of this was to restore the balance between the blue emitting devices and areas such as semi-magnetics and narrow band gap research. Since I am mainly interested in the blue emitting device research, I hope to give you a summary of the work presented only in this area, and I suspect many attending the conference gained a completely different view of the state of current II-VI research.

Notable newcomers on the scene were vertical cavity structures (VCSELs) and a few explorations into the lower dimensional physics of quantum wires and dots were evident. There was a serious attempt by some groups to push emission wavelengths into the UV by continuing to lay the foundations for wider band gap ZnS growth on GaAs and CaF_2. In my opinion ZnS-based light emitting devices are still a long way off.

II-VI blue-green light emitters

Ishibashi of Sony was the first invited speaker, and opened his talk on a very optimistic note by stating that the state-of-the-art MBE grown II-VI wide gap light emitters have characteristics as good as their established III-V counterparts except for lifetimes. At that time Sony's official RT, CW lifetime record was 98 mins, with a threshold current density at room temperature of 1.3 kA / cm^2 at 3-4V. Their latest development in edge emitting technology is an index guided LD grown by what they call one step MBE, which basically means the substrate has a structured GaAs layer so there is no post growth processing to obtain a waveguide. This has decreased the current threshold to 21 mA (350 mA/cm^2) at RT.

As mentioned earlier, the problems associated with short lifetimes were identified 2-3 years ago as p-type dopability, ohmic contacting to p-type layers and material quality problems such as a large intrinsic defect density. Sony made some predictions as to possible solutions to the p-type doping problems based on an increasing effort on semi-empirical theoretical work on the II-VIs. The problem has been investigated simultaneously in Europe by Faschinger, America by Walukiewicz and in Japan by Sony themselves. Both Faschinger and Walukiewicz gave talks at the conference on theoretical limits of the



Blue II-VI lasers.

dopability of II-VI compounds. All adopted a model applied to the III-V compounds in the seventies by Walukiewicz called the amphoteric defect model. Its conclusions are that the dopability of a particular semiconductor, n- or p-type, is dependent on the position of the valence and conduction bands relative to two common energy references, for n- and p- type doping (ESI(n) and ESI(p) respectively. The further these references are into the bandgap, the harder the material is to dope. The doping problem then becomes a question of engineering the band gap to be within these reference levels. Ishibashi suggested the use of ZnSe/ZnMgSSe superlattices as a method of engineering the quaternary band gap to allow higher p-type doping.

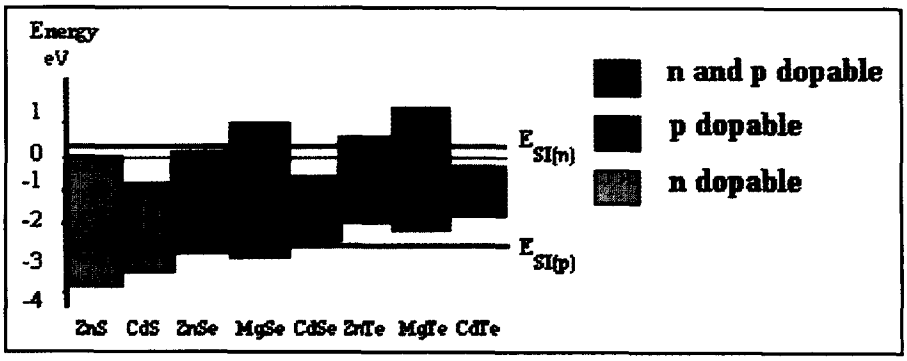
To increase carrier confinement in the present Sony LD structure wider band gap cladding materials are needed, which may point the way to a new generation of II-VI lasers of a larger lattice constant based on the Cd MgSeTe system lattice matched to InAs or GaSb substrates or ZnMgCdSe system using an InP substrate.

Briefly, the final comments from Sony were on their development work on the degradation mechanisms of surface emitting LEDs and conventional edge emitting MOVPE grown devices. Analysis of the degradation process showed that no catastrophically fast degradation occurs. Ishibashi was confident that increased reliability of II-VI laser diodes could be achieved by eliminating preexisting point defects (to prevent the onset of rapid degradation processes) and slowing down gradual degradation by removing point defects from the quaternary-based structure. This work also hinted at the first successful operation of a pulsed-MOVPE grown blue-green laser.

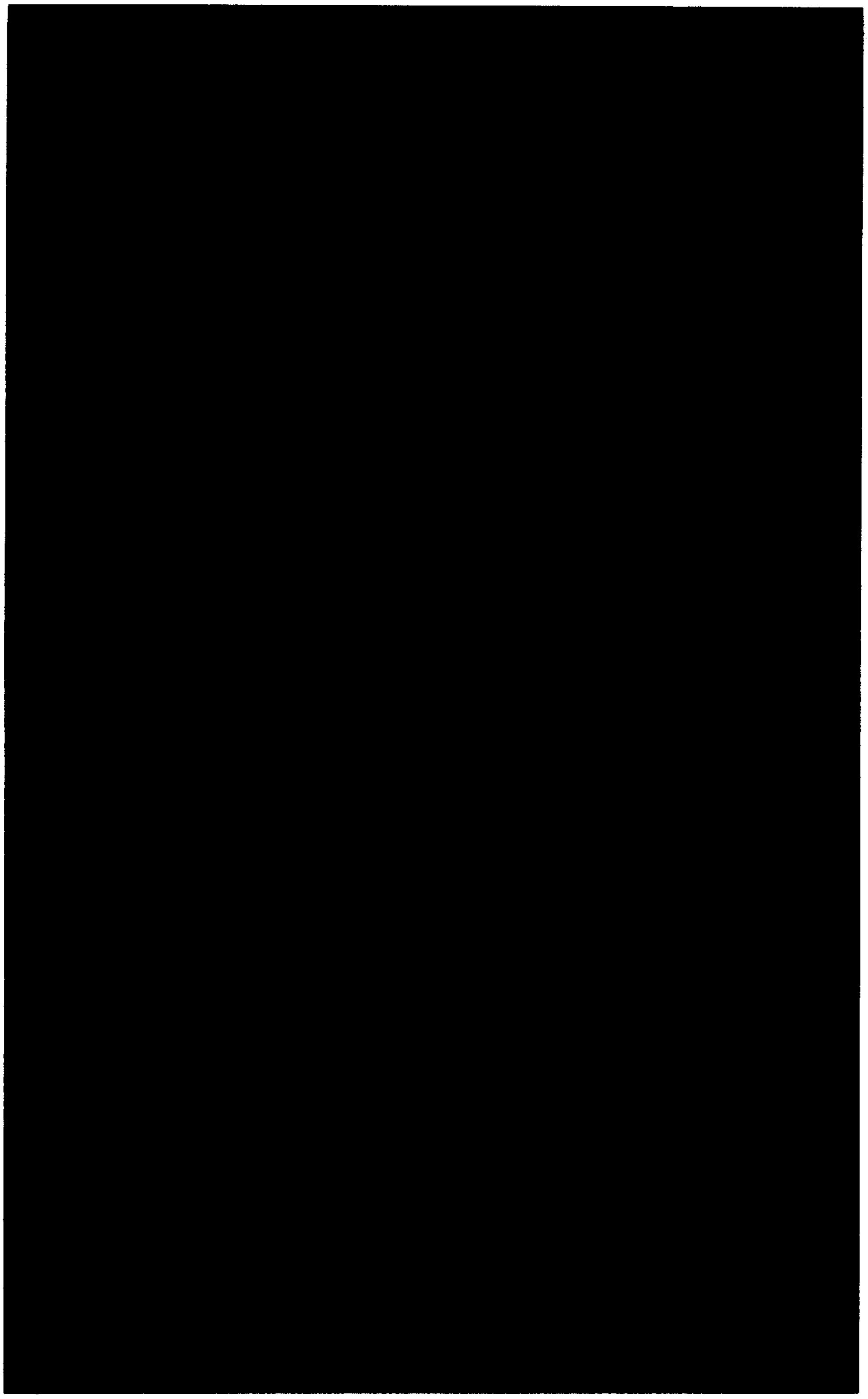
Buffer layers

Contributions from Philips offered no new laser diode design nor any improvement of the lifetime compared to Sony, their longest lifetimes being about 90 mins also. Two studies were presented, a comparison of gain guided and index guided structures, and real time device degradation observation using optical imaging. They concluded that using an index guided structure lowers the threshold current density by a factor of two compared to gain guided structures. The latter study highlighted the problems of growing a completely pseudomorphic device on a GaAs substrate. It is possible to lattice match ZnMgSSe and ZnSSe to the substrate, but in practice fluctuations in compositions occur due to changes in growth temperature and beam fluxes. A value of 0.0015 was quoted as the upper limit of the mismatch in the quaternary layer for a completely pseudomorphic structure. The active region of ZnCdSe and the contact of ZnSe/ZnTe cannot be lattice-matched, but defects in the contacting region are not thought to contribute to the degradation process at the moment, although they could be of consequence as lifetimes increase. The predominant defects in a pseudomorphic structure are stacking faults from the GaAs substrate-epilayer interface. The density of these defects has been decreased by the use of a GaAs buffer layer prior to II-VI growth, but this is still not as good as the $< 10^3$ cm^{-2} density required to increase lifetimes to present III-V values.

Another approach to this problem is to use ZnSe substrates, as reported by Wurzburg. MBE grown LEDs operating at 511 nm were grown on (001) oriented ZnSe substrates, grown by Iodine transport. TEM pictures showed that there are no misfit dislocations at the substrate-epilayer



Relative band positions of the II-VI compounds: W. Faschinger, University of Linz.



Green laser.

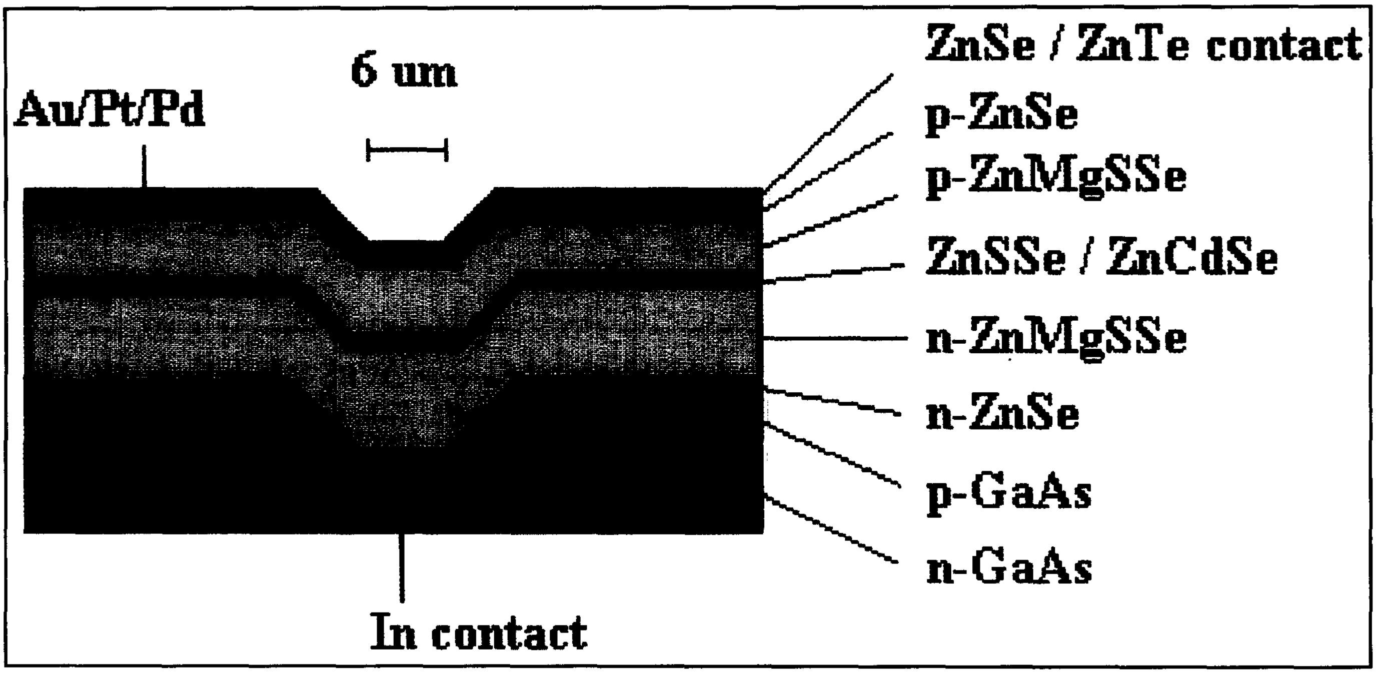
interface, however, dislocations penetrate from the substrate. In this case the substrate quality and dislocation density will dictate the lifetime of the device. Figures of 15- 40 arc sec were quoted for the substrate X-ray diffraction FWHM, and the lowest for an epilayer is 15 arc sec: better than the best values quoted for ZnSe on a GaAs buffer layer (65 arc sec for 150 nm thickness).

MOVPE growth

The invited representative from the II-VI MOVPE community was Gebhardt from Regensburg. He summarised the present state of MOVPE growth of II-VI heterostructures and concluded that it had not yet reached the same maturity or had the same success as MBE growth, the main drawbacks being the lack of a reliable in-situ growth control, low p-type dopability and a lack of good quality control of precursors, a situation little changed from two years ago. He explained that dislocations at the GaAs/ZnSe interface were still a problem, but the dislocation network as viewed by TEM was quite different to MBE grown samples. This was attributed to a 3D growth process rather than 2D as in MBE, more likely due to surface chemistry rather than substrate preparation. Despite these problems the characteristics of a ZnSe/ZnCdSe LED were presented at the last II-VI conference, and as already mentioned Sony has produced a LD grown by MOVPE. More insight into the problem of p-type doping in MOVPE was provided by Yasuda and co-workers. MBE grown nitrogen doped samples were annealed in an activated hydrogen plasma, and then showed significant passivation of shallow acceptors, as observed by PL. This work was complemented by work done at MIT who annealed GSMBE grown material in cracked hydrogen, and came to roughly the same conclusions using CV profiling and SIMS.

Vertical cavity devices

III-V vertical cavity surface emitting lasers (VCSELs) emerged in the late seventies as the brainchild of Iga and co-workers at Tokyo Institute of Technology. Lateral dimensions of the order of 3-20 microns give the potential for better beam profiles and extremely low current threshold densities, as well as the ease of coupling to fibre optics. Until about 18 months ago the II-VI community did not invest any significant time into vertical technology; there were too many fundamental problems with conventional edge emitting geometries to even consider it. Now, already, the problems of achieving electrically pumped vertical structures are being addressed since several groups have demonstrated optically pumped lasing using II-VI active layers and dielectric Bragg stacks. Nurmikko of the Brown-Purdue partnership highlighted the difficulties associated with II-VI epitaxial Bragg stacks, namely composition control and the small differences in refractive index which lead to a large number of high and low refractive index pairs to obtain the 99.97%



Sony LD on a structured substrate.

reflectivity needed. So far in their structures dielectric stacks of SiO_2/HfO_2 have been used. This problem was further highlighted by the first published attempts to grow II-VI stacks by Tampere University. Maximum reflectance achieved is 86 % at 473nm for a MnZnSSe/ZnSSe stack and 81% at 468nm for a ZnMgSSe/ZnSSe stack. Composition variations in sulphur of 1.5% and thickness variations of 6% are reported even with the use of in situ optical monitoring. One must also remember that most of the problems associated with edge emitting LDs must still be tackled in the development of electrically pumped VCSELs since the active region between the mirror stacks is essentially the same. Honda of Tokyo Institute of Technology achieved an optically pumped VCSEL by using a simpler structure than Brown-Perdue, leaving out the quaternary cladding and using a SiO_2/TiO_2 mirror stack. The resulting emission characteristics were not as good as the quaternary cladded VCSEL.

Modulators

All optical telecommunication switching and optical computing have driven III-V research into the field of semiconductor modulators and optical switches. Present II-VI devices which have been demonstrated include self electro optic devices (SEEDs), and work was presented at the conference from the Heriot-Watt Group on piezo-effect optical modulators. Strained ZnCdSe quantum wells grown on (211)B substrates have their optical properties altered due to the internal polarisation fields present in this orientation of the substrate, which produces a blue shift of excitonic transitions with applied bias instead of the usual red shift associated with the quantum confined Stark effect.

Characterisation

In-situ monitoring using reflectance to study growth rates and Raman spectroscopy to examine the strain in epitaxial grown ternaries was popular in the poster sessions, and most of the invited speakers came with good TEM pictures to prove the quality of their samples. There were also isolated studies using more unconventional characterisation techniques such as STM and grazing incidence XRD in a session on surfaces chaired by Prof. Yoshikawa. PL studies of nitrogen doped ZnSe were numerous and identified several new donor and acceptor species such as those seen in delta doped samples presented by Zhu of Heriot-Watt.

The future

The conference confirmed the obvious that there is still a large effort to attain the goal of blue emitting devices with lifetimes which make them commercially viable. Although the materials problems have still not fully been addressed, researchers are already a long way down the road of quality control, and are starting to expand the range of devices which may be available in the future. At the next II-VI international conference in Grenoble in two years time, I would expect this trend to continue, and to see an even larger audience and thicker conference proceedings.

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