R Triboulet and A Rogalski

Professor Robert Triboulet from CNRS, France and Professor Antoni Rogàlski from the Institute of Applied Physics, Military University of Technology in Warsaw, Poland report on the "*Second International Conference on Solid State Crystals (ICSSG) – Materials Science and Applications*", which was held in Zakopane, Poland, 9-13 October and covered developments in bulk crystal growth of GaN and CdZnTe, infra-red detectors for thermal imaging arrays on cars, and two-colour QWIP detectors.

Materials science and applications of solid crystals

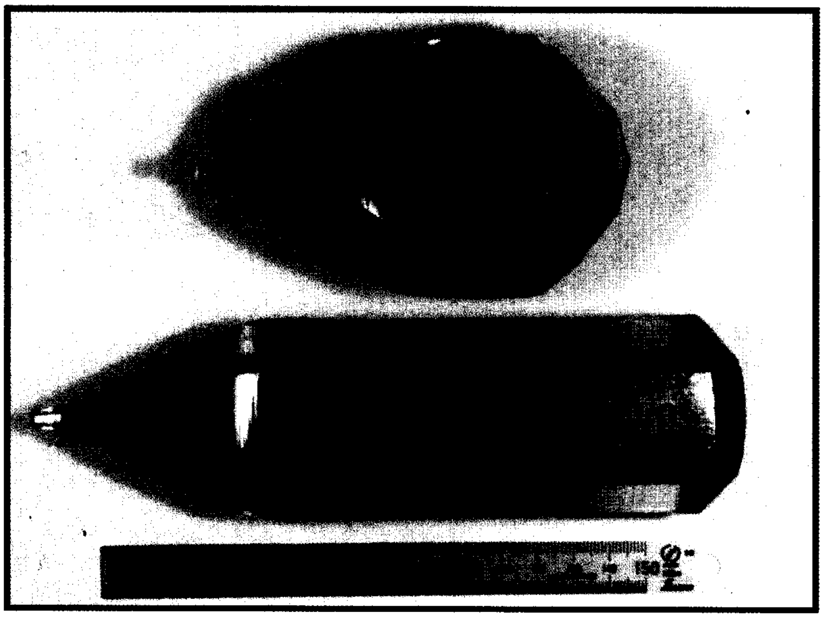


Figure 1. $La_3Ta_{0.5}Ga_{5.5}O_{14}$ single crystals: (a) 3" and (b) 2" diameter.

Out of more than 200 papers presented at the 2nd *International Conference on Solid State Crystals* (including 26 invited lectures, 34 oral presentations and 147 posters, ranging across various families of materials), the majority were focused on III-V semiconductors, including the growth of bulk crystals, thin films, superlattices and nanoscale structures for the fabrication of infra-red detectors (e.g. using InAs/GaInSb), green, blue and ultraviolet detectors and emitters (nitrides), and nanoscale devices.

A second group of papers was dedicated to II-VIs. A particular focus was the use of the HgCdTe ternary alloy as a material for infrared detectors, but also covered were the infrared properties of other IV-VI and II-IV-VI alloys, including PbSe, PbS, (Cd,Pb)Se and PbGeSnTe. Comments on select presentations of interest are included below.

Bulk crystal growth

Fundamental questions such as the problem of striations in crystals for optical applications were addressed by Hans J Scheel of the Swiss Federal Institute of Technology.

Striations are defined as growth-induced inhomogeneities in a crystal which are either aligned along the growth surface or (in the case of faceted growth) related to the traces of macrosteps. These often periodic inhomogeneities are caused by growth rates which fluctuate with time or by lateral growth rate differences along the growth interface.

In the majority of cases the striations can be eliminated by control of the interface shape, either by adjusting its continuous curvature or by a flat interface achieved by a transition to faceting. The key is to prevent macrostep formation and lateral growth rate differences.

R Triboulet of the Laboratoire de Physique des Solides et de Crystallogenese (France) discussed the "old" semiconductor zinc oxide (ZnO), including its attractive physical properties that distinguish it from other wide-gap semiconductors, in particular gallium nitride. Interest in this material has now reactivated, as it has again become topical for applications related not only to its optoelectronic capabilities in the ultraviolet range but also to its piezoelectric properties for developing surface acoustic wave (SAW) filters to be integrated in future analogue circuits for portable electronic. Research into its bulk growth includes the use of activated sublimation, chemical vapour transport, and thin-film MOCVD growth methods.

The development of new crystal materials and new materials forms for electro-optical applications was presented by T Fukuda of the Institute for Materials Research, Tohoku University (Japan).

For many practical applications such as medical procedures, semiconductor processing, optical communications and remote sensing, fluoride single crystals ($LiCaF$, $LiSrAlF_6$, $YLiF_4$, $LuLiF_4$) are of practical importance. New piezoelectric crystals for electronic applications - LGS ($La_3Ga_5SiO_{14}$), LNG ($La_3Nb_{0.5}Ga_{5.5}O_{14}$), LT ($LiTaO_3$) - have superior properties such as zero temperature coefficients and large electromechanical coupling factors.

Figure 1 shows the as-grown LTG single crystals of approximately 2" and 3" diameter. Using LGS single crystals, monolithic-type filters (10.4 and 21.4 MHz) with lower input and output impedance, smaller size, and lower attenuation than those made of quartz were made.

For single-crystal fibres, a superior growth technique - the micro pulling-down method - has been developed. This method enables the fabrication of new, high-quality fibres of oxide, semiconductor and ceramic matrix composites with high melting temperature and/or incongruent melting composition. High tensile strength (580 MPa) at elevated temperature (1500°C) - three times as high as that of bulk material - was achieved for $Al_2O_3/Y_3Al_5O_{12}$ eutectic fibres.

A Mycielski of the Institute of Physics, Polish Academy of Sciences discussed requirements for the growth of very-high-quality crystals of wide-gap II-VI semiconductors (mainly CdZnTe) for applications such as transparent substrates for subsequent LPE, MBE and MOCVD HgCdTe epilayer deposition and for x-ray and gamma-ray detectors.

Recent advances in CdZnTe growth techniques have made it possible to realise room-temperature radiation detectors with good energy resolution and sensitivity. Using a new technique - the high-pressure vertical Bridgman (HPVB) process - it is possible to produce large-size CdZnTe with resistivity up to 10^{11} Ω cm, which results in lower leakage current in MSM and p-n junction photodiodes. The HPVB-grown CdZnTe also facilitates these thicker devices because of the much-larger ingot obtained from the growth process, and large ingots lead to economies of scale and lower costs for CdZnTe compared to CdTe. These results have rekindled interest for CdZnTe detector applications in which high-energy resolution is critical.

Epitaxial layers

M Razeghi of the Center for Quantum Devices, Northwestern University (USA) discussed the status of currently available infrared lasers and detectors and the advantages and disadvantages of different fabrication techniques. Although impressive progress has been achieved, microelectronics is still far from being able to imitate natural structures such as molecules and human brain cells in terms of integration density, functionality and performance. The challenges facing semiconductor technologies in the new Millennium will be to move towards nanoscale devices which will be characterised by their high integration density, high speed and low power consumption. Lower-dimension devices, like quantum wires and quantum dots, can dramatically improve the performance of infrared lasers and detectors, but in the near future it is foreseeable that even artificial atoms, molecules, and integrated multi-functional nanoscale systems can be created.

The most successful method for growing GaN single crystals is the high-hydrostatic-pressure, high-temperature method, detailed by the research team from the High Pressure Research Center UNIPRESS (Poland). At present the crystals are of size 100 mm^2 and dislocation density $< 10^3$ cm^{-3}. After mechanical polishing and reactive ion etching, the crystals are suitable as substrates for AlInGaN epitaxy.

M Leszczynski of UNIPRESS presented the usage of such GaN substrates for the fabrication of AlGaN epitaxial layers using MOCVD, including an ultra-narrow photoluminescence line (about 0.1 eV) for GaN and a small threshold for stimulated emission. Figure 2 shows the stimulated emission from a GaN homoepitaxial layer pumped using an excimer laser. The half-width of the electron-hole plasma peak is less than 3 meV, i.e. about three times less than for GaN layers on a sapphire substrate.

Z Zytkiewicz of the Institute of Physics, Polish Academy of Sciences summarised recent progress in epitaxial lateral overgrowth (ELO) selective epitaxy on partially masked substrates. The most spectacular achievement of this technique is the significant improvement in performance of GaN/InGaN blue laser diodes due to the filtration of lattice misfit defects during lateral overgrowth. Although the ELO layers are structurally of much higher quality than the planar

Using a new technique - the high-pressure vertical Bridgman process - it is possible to produce large-size CdZnTe with resistivity up to 10^{11} Ω cm, which results in lower leakage current in MSM and p-n junction photodiodes...Large ingots lead to economies of scale and lower costs for CdZnTe compared to CdTe.

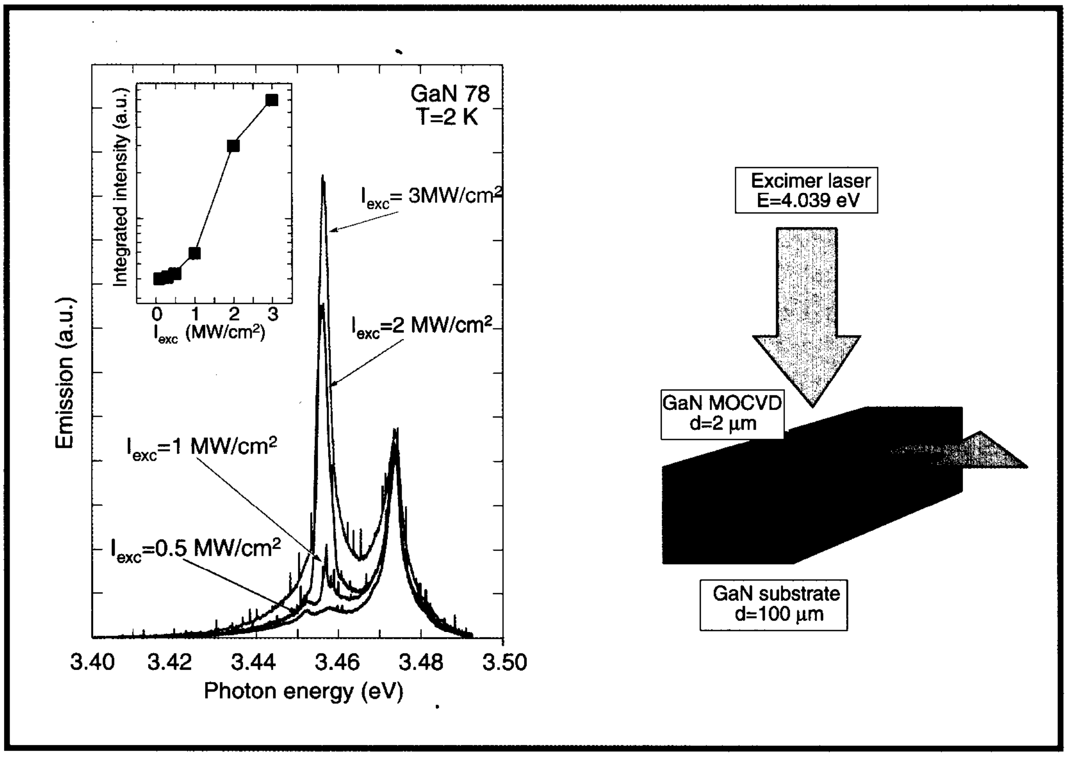
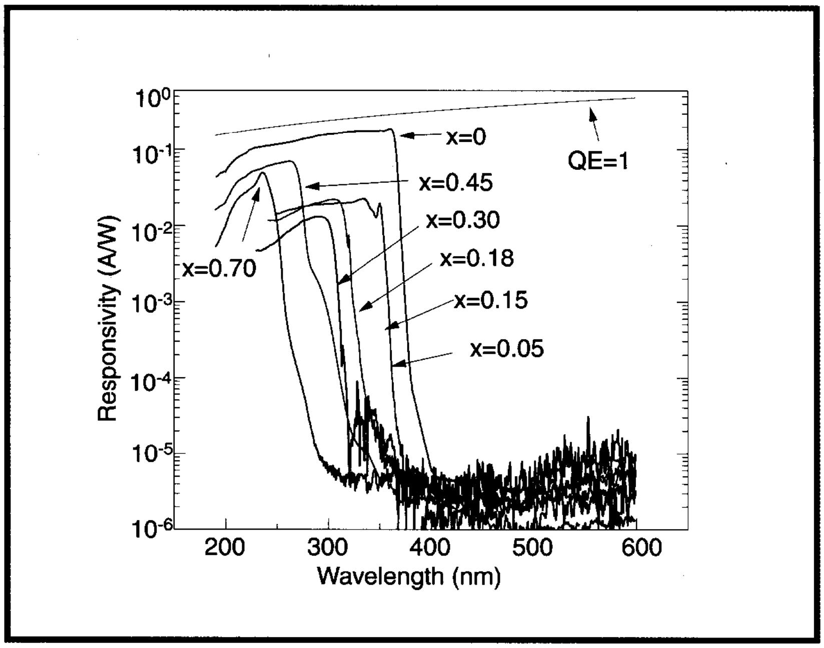


Figure 2. Stimulated emission from GaN layer grown by MOCVD on GaN single crystal.

layers deposited directly on the substrate, they are not free of strain and/or other distortion. The sole role of an amorphous mask in ELO is to ensure high growth selectivity. It appears that by adjusting the parameters of the GaAs ELO system grown by liquid phase epitaxy on GaAs and GaAs-coated Si substrates, the adhesion-induced strain in the ELO structures can be significantly reduced. It was also shown that, during the growth of the GaAs ELO layers on Si substrates, there is a significant influence of the lattice and thermal expansion coefficients mismatch on the deformation of the ELO lattice planes.

Figure 3. Responsivity of $Al_xGa_{1-x}N$ p-i-n photodiodes showing a cut-off wavelength continuously tunable from 227 nm to 365 nm, corresponding to Al concentration in the range 0–70%.



Optoelectronic devices

Many of the presentations described improvements in the performance of optoelectronic devices, especially photodetectors.

Yoon-Soo Park of the Office of Naval Research (USA) reviewed the demonstration of commercial high-brightness blue and green LEDs and violet laser diodes. However, improvements will extend the usage and efficiency of these new light sources (e.g. to white-light LEDs), increase the density of optical data storage, and enhance environmental awareness capabilities (e.g. through ultraviolet and visible photon detectors and sensors).

Figure 3 shows the current responsivity of AlGaN p-i-n photodiodes with a cut-off wavelength continuously tunable from 227 to 365 nm (corresponding to Al concentration in the range 0–70%). Their internal quantum efficiency was up to 86% and they exhibited an ultraviolet-to-visible rejection ratio as high as six orders of magnitude.

A Rogalski of the Institute of Applied Physics, Military University of Technology (Poland) overviewed progress in infrared detectors and the outlook for near-future trends in IR technology. Future applications of IR detector systems require:

- higher pixel sensitivity;
- a further increase in pixel density to above 10^6 pixels;

- cost reduction in IR imaging array systems through the use of sensors that don't need to be cooled to such low temperatures, combined with the integration of detectors and signal processing functions (with much more on-chip signal processing); and
- improvement in the functionality of IR imaging arrays through the development of multi-spectral sensors.

Sales of IR thermal imaging equipment to the automobile market are forecast to start rapidly changing the ratio between military/government and commercial IR markets. Today only about 10% of the market is commercial, but over the next decade this could grow to over 70% in volume and 40% in value, largely through volume production of uncooled imagers for automobile driving aids, for which the cost would decrease to below US$1000. Of course, these systems will also cover other segments of the transportation industry: trucks, trains, ships, barges, buses, and aeroplanes.

S D Gunapala of the Jet Propulsion Laboratory, California Institute of Technology (USA) discussed the effect of focal plane array non-uniformity on the performance, optimisation of the detector design, material growth and processing that has culminated in the realisation of a large-format long-wavelength QWIP camera, which shows great promise for many applications in the 6-18 μm wavelength range in science, medicine, defence and industry.

He also presented recent developments in two-colour QWIP integrated chips based on the AlGaAs/GaAs material systems, which allows the simultaneous detection of the 8-9 and 14-15 μm spectral bands. Figure 4 shows simultaneously acquired images using the two-colour camera. For long-wavelength and very-long-wavelength detectors at 40 K the estimated values of NEDT (noise equivalent difference temperature, i.e. the difference in the temperature of the object required to produce an electric signal equal to the rms noise voltage) are 36 and 44 mK.

F Szmulowicz of the Air Force Research Laboratory, Wright-Patterson AFB (USA) discussed progress in optimising the performance of p-type GaAs/AlGaAs QWIPs through modelling, growth, and characterisation. Whereas n-QWIPs require extra processing for gratings in order to absorb normally incident radiation, p-QWIPs intrinsically allow such absorption. Using the 8↔8 envelope-function approximation, a number of structures were designed and their optical properties calculated for comparison with experimental data. Resonant-cavity devices were grown by MBE based on the theoretical designs and their photo-response measured. The quantum efficiencies and the background-limited detectivities were comparable to those of n-type QWIPs. However, the responsivities were smaller. At 80 K, the detectivity of the optimum-doped sample was 3.5×10^{11} cmHz$^{1/2}$W^{-1} at 10 V bias.

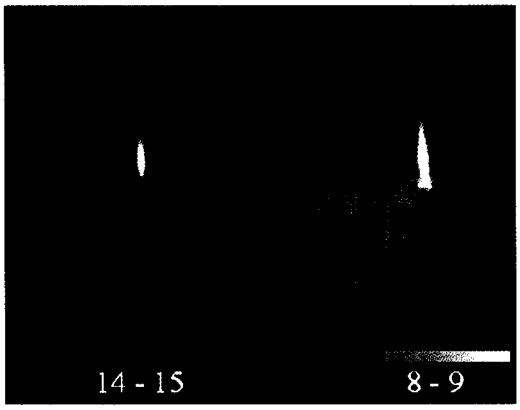


Figure 4. Two-colour images of a flame simultaneously acquired with a 640x486 two-colour QWIP camera: (left) 14-15 μm infrared; (right) 8-9 μm infrared. The pixel pitch of the Focal Planar Array is 25 μm. The 14-15 μm image is less sharp due to the diffraction-limited spot size being larger than the pixel pitch of the FPA.

Several presentations at the conference focused on III-V compound semiconductors and type II superlattices containing antimony (Sb).

InGaAsSb quaternary alloys can provide room-temperature photodetectors operating in the wavelength range 1.9-2.4 μm, depending on alloy composition. T Piotrowski of the Institute of Electron Technology (Poland) outlined recent progress in the fabrication of GaSb/n-InGaAsSb/p-AlGaAsSb LPE heterojunction photodiodes operating in the 2-2.4 μm wavelength region. The photodiodes were characterised by a zero-bias-voltage resistance-area R_0A product up to 400 Ωcm^2 and detectivity in the range 3×10^{10}-2×10^{11} cmHz$^{1/2}$W^{-1} (depending on the cut-off wavelength).

Compared to the Type I superlattice structures, Type II structure offers the advantages of greater electrical confinement and reduced Auger recombination, loss mechanisms that have seriously hampered the development of room-temperature continuous-wave devices. These fundamental phenomena were considered by R J Nicholas of the Department of Physics, Oxford University (UK). The high performance of InAs/InGaSb strained-layer-superlattice detectors is a result of longer carrier lifetimes caused by the splitting of the light-hole and heavy-hole bands. Recombination in strained-layer superlattices occurs by a relatively slow Auger recombination process.

Today only about 10% of the [IR thermal imaging] market is commercial [i.e. non-military/government], but over the next decade this could grow to over 70% in volume and 40% in value, largely through volume production of uncooled imagers for automobile driving aids.

Acknowledgement

The ICSSG conference was financially supported by the Committee for Scientific Research (KBN), European Office of Aerospace Research and Development, SPIE - The International Society for Optical Engineering, Institute of Physics Technical University of Lódz, and the Institute of Physics Wroclaw University of Technology.

The event attracted over 200 participants from 20 countries (mostly from Eastern Europe - but forming a forum for the discussion and exchange of information between eastern and western delegates - and an increase on the 140 delegates in 1996 and the 170 in 1998).A clear effort has to be undertaken to strengthen these two delegations, which requires more financial support to welcome people from eastern countries.

This second event followed the *1st International Conference on Solid State Crystals (ICSSG)* - *Materials Science and Applications*" Zakopane, Poland in October 1998, which was preceded by the *12th Symposium on Solid State Crystals: Materials Science and Applications* in October 1996.

* Papers presented at the 2nd ICSSG conference will be published in a special issue of the SPIE Proceedings and in the journal *Opto-Electronics Review*.

Contact:
R Triboulet
CNRS, Laboratoire de Physique, des Solides de Bellevue1, Place A. Briand, F-92195 Meudon Cedex, France
Fax: +33-1-45075841
E-mail: triboulet@cnrs-bellevue.fr

and

A Rogalski
Institute of Applied Physics, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland
Tel/Fax: +48-22-695-9109
E-mail: rogan@wat.waw.pl