

SYNTHESIS REPORT

FOR PUBLICATION

CONTRACT N°:

BE-7698-93

PROJECT N°:

BRE2-CT93-0586

TITLE :

MOVPE Growth and Optoelectronic Characterization of
II-VI Blue-emitting Materials (BLUEMAT)

PROJECT
COORDINATOR :

Epichem Limited

PARTNERS :

Université de Liège
Imperial College
RWTH Aachen
Universidade de Aveiro

STARTING DATE : 1 November 1993

DURATION : 36 MONTHS



PROJECT' FUNDED BY THE EUROPEAN
COMMUNITY UNDER THE BRIT/ EURAM
PROGRAMME

DATE :

17 December 1996

MOVPE Growth and Optoelectronic

Characterization of II-VI

Blue-emitting Materials

BLUEMAT

BE-7698-93

SYNTHESIS REPORT

Contributors: Epichem Limited

University de Liege

Imperial College

RWTH Aachen

Universidade de Aveiro

Editor: MEG

Authors

Simon Rushworth
Epichem Limited
Power Road, Bromborough
Wirral
UK L62 3QF Merseyside

Prof. Anthony **Jones**
Rose Tree Cottage
Georgia Close
Eccleston Park
UK-L35 7JW Prescot Merseyside

Prof. Roger Evrard
Université de Liege
Laboratoire de Physique des Solides
Institut de Physique
SART TILMAN
B-4000 Liege 1

Prof. Paul O'Brien
Dr. **Azad Malik**
Imperial College of Science, Technology and Medicine
Department of Chemistry
South Kensington, London
UK-SW72 AY

Dr.-Ing. Michael Heuken
Mr. Wolfgang Taudt
RWTH Aachen
Institut für Halbleitertechnik
Lehrstuhl I
Templergraben 55
D-52062 Aachen

Prof. Heiena Nazaré
Mr. (laude Boemare
Universidade de Aveiro
Departamento de Física
Campo Universitário
P-38(30 Aveiro

Table of Contents

1.	Abstract	4
2.	Introduction	4
3.	Technical Description	5
4.	Results	8
5.	Conclusions	13
6.	Acknowledgments	14
7.	References	14

1. Abstract

The overall aim of the project was to develop successful technology for the production of ZnSe and ZnSSe optoelectronic devices by MOVPE. The optimum precursors combination for the growth of ZnSe, ZnSSe and ZnMgSSe has been identified as $\text{Me}_2\text{Zn}(\text{NEt}_3)$, $\text{t-Bu}_2\text{Se}$, $\text{t-Bu}_2\text{S}$ and $(\text{MeCp})_2\text{Mg}$. By the use of a nitrogen plasma, or the nitrogen-containing precursors $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{EtZnN}(\text{SiMe}_3)_2$, nitrogen has successfully been incorporated into ZnSe at the level of approx. 10^{17} cm^{-3} . However, the layers did not show p-type conductivity due to compensation of the nitrogen by n-type impurities (chloride) or passivation by hydrogen. Lattice-matched ZnMgSSe was successfully grown as GaAs and quantum-size effects were observed. Optical and electron beam pumped blue green lasers at room temperature were also demonstrated.

2. Introduction

Wide band gap II-VI materials, such as ZnSe ($E_g = 2.6 \text{ eV}$) and ZnS ($E_g = 3.7 \text{ eV}$), have a large potential application in optoelectronic devices operating in the blue/green region of the visible spectrum. However, in the past, progress has been severely limited by the tendency of II-VI materials to form defects and interdiffuse at temperatures above 500°C ; by a lack of material lattice-matched to substrates; and by difficulties in p-type doping.

The aim of the project was to develop a successful technology for the production of ZnSe and ZnSSe optoelectronic devices by metalorganic vapour phase epitaxy (MOVPE). Alternatively, it was intended to fully define the important chemical and materials parameters that determine the feasibility of producing "real world" ZnSe-based devices by MOVPE. In order to achieve this, improvements were required in a number of key, and interrelated, technological areas including precursor design and manufacture, II-VI epitaxial layer growth, and layer characterization.

A number of objectives were defined, as follows;

- (i) Manufacturing and purification routes to Zn, Se and S metalorganic precursors must be improved to enable the growth of high purity ZnSe and ZnSSe, free from extrinsic dopant impurities. In particular, the metalorganic precursor should not contain any halide impurities, which are efficient n-type dopant sources.
- (ii) The optimum combination of Zn, Se and S precursors must be identified, which will allow the growth of II-VI layers at a sufficiently low temperature (between $330\text{-}360^\circ\text{C}$) for successful p-type doping.
- (iii) Techniques must be found to overcome the lattice mismatch between ZnSSe layers and the commonly used substrate GaAs.

- (iv) Improved techniques must be developed for the electrical and optical characterization of the ZnSe and ZnSSe layers, so that the effectiveness of the new precursor and growth technologies can be assessed.
- (v) Perhaps most crucially, reliable and reproducible n- and p-type doping must be obtained.

Although n-type doping is readily achieved using alkyl halides, p-type doping has proved to be a particular problem in MOVPE. Nitrogen is the most promising p-dopant in ZnSe/ZnS materials [1 -4] and thus new, more effective nitrogen dopant sources need to be developed.

These objectives were largely met through a work programme based on clearly defined roles for each partner.

Epichem manufactured conventional precursors (e.g. $\text{Me}_2\text{ZnNEt}_3$, R_2Se , R_2S , etc.) using improved routes aimed at reducing impurities in the precursor. Then precursors were fully characterized, using ICP-ES, ICP-MS, proton NMR, and supplied to RWTH Aachen for the MOVPE growth of ZnSe, ZnSSe and ZnMgSSe epitaxial layers on GaAs substrates. Imperial College carried out the small scale synthesis of novel precursors, and investigated precursors containing a direct [Zn-N] bond, to enable nitrogen-doping **to be more easily achieved**. These novel precursors were then synthesized on a larger scale at Epichem. After full characterization, the new sources were supplied to RWTH Aachen for assessment as nitrogen dopant sources. Imperial College also carried out extra characterization (e.g. vapour pressure measurements, high resolution NMR) on precursors prepared at Imperial College and Epichem. The quality of the II-VI heterostructures was assessed using optical methods (Universidade de Aveiro) and electrical methods (University de Liège). These results were fed back to RWTH Aachen and Epichem to enable iterative improvements to be made in layer growth methods and precursor manufacturing technology.

3. Technical Description

In order to achieve the project objectives, a number of **specific tasks were identified**. These were as follows:

Task 1: Precursor development

The first goal of Task 1 was to identify and produce the optimal precursors for reproducible deposition of high purity ZnSe and ZnS layers, a prerequisite for any doping studies. Therefore, in order to allow RWTH Aachen to reach this goal, Epichem's initial efforts concentrated on the production of ultra pure batches of optimised Zn, Se, and S source materials.

The properties of ideal precursors for high quality ZnSe deposition include access to lower growth temperatures, precursor compatibility i.e. no pre-reaction. **Epichem's predominant**

aim was to produce ultra pure source materials. $t\text{Bu}_2\text{Se}$ was chosen for two reasons: firstly from a deposition viewpoint, as substrate temperatures around 330°C may be employed which is lower than the temperatures required for other Se sources. Secondly, from a synthesis viewpoint, a novel halide-free route could be applied during precursor production, yielding significantly higher quality product.

Similarly, $\text{Me}_2\text{Zn}.\text{NEt}_3$ was chosen due to the availability of a route yielding ultrahigh purity product. Again $t\text{BuSH}/t\text{Bu}_2\text{S}$ were chosen for the above properties to establish the optimum precursor combination to ensure the highest quality films were deposited.

Having identified halide contamination as the major problem with li-Vi precursors, synthetic routes and purification methods have been developed at Epichem to minimise the levels of these elements in the final products. A key result of this effort is that Epichem has succeeded in producing ditertiarybutylselenium of higher purity than currently available commercially. Further success in the production and supply of ultra high purity dimethylzinc.triethylamine adduct, tertiary butylthiol, and ditertiarybutylsulphide have allowed RWTH Aachen to deposit excellent quality layers in a controlled manner.

Another key objective of the project was to obtain precursors suitable for p-type doping of ZnSe. The most promising dopant for p-type doping of ZnSe is nitrogen [1-4]. Simple nitrogen-containing sources such as NH_3 cannot be used for doping since hydrogen will also be incorporated into the layers causing deep centres and compensation effects. To achieve high doping levels, a low deposition temperature is required. Therefore, it was considered vital to **investigate the synthesis of nitrogen-containing metalorganics with the potential of a low decomposition temperatures.** Zincalkylamides are good candidates as precursors [5,6], but until this project commenced, they had not been adequately assessed with regard to vapour pressure, purity, and deposition characteristics.

An objective of task 1 was to synthesize new zincalkylamides with properties suitable for being used as zinc sources. To attain this aim, simple alkylamides were first synthesized at Imperial College, purified by using a variety of methods, characterized in terms of structure and purity, the vapour pressure was measured, and samples were supplied in small quantity to Epichem for further evaluation and scale-up. After some feedback about the performance of the precursors, more complex precursors were synthesized to enhance good properties. They were purified, characterized completely, and their vapour pressure was measured. Again, Imperial College supplied preferred precursors with full vapor pressure data and synthetic method to Epichem.

A number of nitrogen doping sources have been investigated at Epichem in addition to the alkylamide precursors identified by IC. Batches of all these materials have been supplied to RWTH Aachen for evaluation and further scale up of the most promising compound was performed.

A final objective of Task 1 was to investigate the adduct precursors and to develop existing sulphur and selenium precursors and transfer the technology to Epichem for the scale-up of the preferred precursors. Scale up of the routes developed above will allow Epichem to compete in the world market for all II-VI source compounds.

Task 2: Epitaxial growth and Initial characterization of H-VI films

For the production of optoelectronic devices operating in the blue spectral region of the light, ZnSe-based material were used. The aim of this project is to solve the arising problems which were related to a special growth method used for industrial production: metallorganic vapour phase epitaxy. . The problems **can be** separated into three important parts:

- optimization of the growth process to achieve the required electrical, optical and structural quality of the undoped layers
- achievement of reproduceable and high p-type and n-type conductivity. Special problems are connected with the p-type doping
- enhancement of the efficiency of the optoelectronic devices. Improvement of the structural quality of the layers to minimize the degradation effects of the devices to increase device lifetime

Furthermore, there are several problems connected with the task of the purity of the precursors and electrical contacts and measurements.

Task 3: Optical characterization of grown materials

The objective of Task 3 was to use optical tools, namely photoluminescence, reflectivity, and photoreflectivity, to non-destructively characterize heterostructures, QW, and MQW as well as the basic materials (ZnSe, ZnSSe, ZnMgSSe) used to fabricate the optical devices.

With this characterization, Aveiro aimed at establishing a correlation between the growth parameters and the optical quality of the material and to provide information to help design the optically active components of the devices.

Task 4: Electrical characterization

The electrical characteristics of the optical layers were attained by Liège via the following methods:

- determination of concentration and profile of active electronic traps in the epitaxial layer
- obtainment of correlation between the trap concentrations and the growth conditions
- determination of the density of interface states at the GaAs-ZnSe junction and its correlation with the different growth conditions
- determination of the relation between the preparation method of the metal contacts on the epitaxial layer and their electrical characteristics
- establishment of new methods for preparing low-resistance ohmic contacts on ZnSe.

Task5: Correlation of precursors to film quality

The objective of this task was to identify critical parameters affecting the deposition of high quality ZnSe. Furthermore, by monitoring this information, improvements in the production process could be made, thereby ensuring films of increasingly higher purity were deposited.

The correlation of electrical and optical properties of films deposited employing novel precursors prepared by proprietary routes was crucial for **assessing** the progress achieved over commercially available source materials. By thoroughly understanding the characterization data for grown layers, improvements in film quality could be monitored and related back to changes in growth conditions, source materials employed, and further to precursor purification methods and impurity levels. Due to the very low levels of contamination required to seriously impair film quality, assessment of all aspects of the production process were monitored by the appropriate techniques to determine which parameters increased film quality. These areas were targeted to optimize the quality of deposited films.

In particular, precursor analysis performed at Epichem was compared with the properties of films grown employing the same material to ensure precursor quality can be judged prior to shipment. Also, development of purification techniques is dependent on accurate analytical data to assess efficiencies.

Metals analysis, using ICP-ES/MS analysis, was performed on all the precursors prepared at Epichem and supplied to consortium members. Proton NMR has also been performed on several samples to ensure solvent contamination is not present in the final product.

4. Results

4.1 Precursor Development

4.1.1 Conventional Sources

Growth results from RWTH Aachen showed that dimethylzinc triethylamine, $\text{Me}_2\text{ZnNEt}_3$, was the preferred zinc source. It has a convenient vapour pressure for MOVPE (18 Torr at RT), and the presence of NEt_3 reduces halide contamination. It is also free from pre-reaction with Se or S precursors.

Epichem developed a method of analysing (using ICP-MS) for low levels of halide impurity, which indicated that volatile partially alkylated species (MeZnX) remained in the $\text{Me}_2\text{ZnNEt}_3$ source. Subsequent modification of the synthesis route led to improved purity $\text{Me}_2\text{ZnNEt}_3$.

Group VI Sources (Epichem Ltd)

A range of Se and S sources were synthesized by Epichem and supplied to RWTH Aachen. These included diethylselenium (Et_2Se), diisopropylselenium ($i\text{-Pr}_2\text{Se}$), ditertiarybutylselenium ($t\text{-Bu}_2\text{Se}$), tertiarybutylthiol ($t\text{-BuSH}$) and ditertiarybutylsulphide ($t\text{-Bu}_2\text{S}$).

t-Bu₂Se was identified as the most suitable source for low temperature growth of ZnSe and a novel “halide-free” route was developed by Epichem. Purification routes were also developed for t-BuSH and t-Bu₂S.

Mg Sources (Epichem Ltd)

Initially, the solid Mg source Cp₂Mg was supplied by Epichem to RWTH Aachen. However, problems in the reproducibility of vapour transport, (due to solid redistribution in the source container, led to the development of the new source (MeCp₂)Mg (liquid at 40°C).

Nitrogen Dopant Sources (Epichem Ltd)

Epichem also supplied RWTH Aachen with two potential nitrogen dopant sources for evaluation. Trimethylsilylazide (Me₃SiN₃) was proposed by Epichem whilst triallylamine (allyl₃N) has recently been reported by W. Gebhardt’s group at Regensburg University.

Furthermore, the adduct Me₂Zn.allyl₃N was supplied to RWTH Aachen for assessment as a dopant material.

4.1.2 Novel Nitrogen Sources (Imperial College)

Work by Rees et al [5,6] indicates that zinc dialkylamides of the type Zn[NR₂]₂ (R = Me, Et, ‘Pr, Me₃Si - etc.] are promising nitrogen dopant sources. Therefore, 27 compounds of this type were synthesized at Imperial College [see Table 1].

The most promising precursors identified were bis(di(trimethylsilyl)amido)zinc, Zn(N[SiMe₃]₂)₂ and ethylzincdiisopropylamide, EtZnNⁱPr₂. A novel purification route was developed for Zn(N[SiMe₃]₂)₂ involving the formation of a pyridine adduct, followed by thermal dissociation to give the purified Zn(NR₂)₂ species.

4.2 Growth of Undoped ZnSe Layers

In order to minimize defect formation, as well as to increase the concentration of nitrogen dopant in the ZnSe/ZnS layers, it is necessary to use low growth temperatures (i.e. < 350°C). A range of Se and S precursors were investigated (see Table 2), and ditertiarybutyl selenide (t-Bu₂Se), tertiarybutylthiol (t-BuSH) and ditertiarybutyl sulphide (t-Bu₂S) were found to give the lowest growth temperatures (T_o - 330°C).

The optimum precursor combination and growth conditions were as follows:

Zn precursor	Me ₂ Zn(NEt ₃)
Se precursor	t-Bu ₂ Se
Growth Temp	300- 340°C
Pressure	atmosphere
VI/II ratio	0.2

Detailed electrical and optical characterization showed that halide (probably Cl) was an impurity in the ZnSe layers, leading to a high n-type background. After further purification of the Zn and Se precursors, the following optimized layer properties were obtained:

- **FWHM of the I_2 emission line** (sample thickness: 4.6 μm): 1.9 meV
- carbon and hydrogen incorporation below detection limit of SIMS
[C: $1 \times 10^{16} \text{ cm}^{-3}$ and H: $2 \times 10^{17} \text{ cm}^{-3}$]
- **FWHM of (400) reflex** in X-ray rocking curve: 0.044° for a 0.1 μm thick sample
- the n-type background concentration in the layers could be reduced from $1 \times 10^{17} \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$
- (Note: this was achieved at a “growth temperature of 330°C. It would be easy to reduce the background concentration by using higher growth temperatures, **BUT then it will be impossible** to dope.)

4.3 Growth of n- and p- doped ZnSe layers

ZnSe-based optoelectronic devices require p/n junctions. n-type doping has been successfully achieved using n-butylchloride (n-BuCl), **leading** to free electron concentrations of $2 \times 10^{18} \text{ cm}^{-3}$ in ZnSe and $1 \times 10^{17} \text{ cm}^{-3}$ in ZnSSe lattice-matched to ZnSe.

However, p-type doping in ZnSe is very difficult to achieve. **MBE studies** have shown that nitrogen is the optimum p-type dopant in ZnSe and two methods of incorporating nitrogen were investigated in this project: DC-plasma doping and doping with nitrogen-containing chemicals.

4.3.1 Plasma Doping

The idea of the plasma doping is to transfer the successful plasma doping process carried out in MBE to the MOVPE process. With plasma, the inert nitrogen gas can be activated, which should result in a nitrogen incorporation in the layers. With RWTH Aachen's equipment, only a DC-plasma activation was possible in a low pressure MOVPE system.

For the doping, an additional nitrogen flow was activated by DC plasma. For each Se and Zn precursor combination tested, RWTH Aachen observed that a decrease of the growth temperature results in a higher concentration of nitrogen in the layers. This could be concluded from the increase of the intensity ratio between the donor acceptor pair emission (DAP) correlated to nitrogen and the excitonic emissions. At high concentrations, the DAP emissions and their phonon-replica dominated in the PL spectra, the full-width-half-maximum of this lines were broadened, and the peak maximum was shifted towards lower energies. Additionally, the intensity ratio between the nitrogen acceptor correlated 1_1^N emission line and the donor bound I_2 excitonic emission lines increased, before both excitonic lines nearly vanished in comparison to the DAP emissions. This is in accordance with published results for MBE-grown p-type conducting ZnSe:N samples.

All of the nitrogen-doped ZnSe layers were semiinsulating, if they were grown at high temperatures. At growth temperatures of 330°C with DTBSe as Se-precursor, most of the

layers were n-type conducting. The group concludes that this is due to a high chlorine background doping. In experiments with different nitrogen flows, it was shown that the nitrogen content in the layers could be controlled by this parameter.

For an increased nitrogen flow, the PL spectra show an increase of the nitrogen concentration in the same way as for a decreased growth temperature. The maximum free electron concentration was reduced by an increased nitrogen concentration in the layers. When the nitrogen concentration was further increased, the layers became semiinsulating. In SIMS measurements, hydrogen was found in the layers. RWTH Aachen explains the semiinsulating behavior with hydrogen passivation, if the acceptor concentration exceeds the concentration of donors. For the highest nitrogen concentration in the layers, n-type conductivity was observed again, which can be explained by the donor-like behavior of nitrogen complexes created at high concentrations.

With a higher purity selenium sources, the n-type conductivity of the low-doped layers was reduced, which clearly shows that the background doping was responsible for the n-type conductivity if the concentration of nitrogen in the films is low. Therefore, with one of the purest Se batches, all the layers were semiinsulating. By comparing this result with the SIMS measurements, one can infer hydrogen passivation of the layers.

All the layers grown with this method exhibit excellent PL behavior. They are comparable to MBE-grown samples. Only the fact that nitrogen-doped layers with a small Cl background contamination are semiinsulating and not p-type conducting indicates the need to investigate the doping process with different methods. Additionally, it might be that the DC plasma activation of elemental nitrogen creates a nitrogen species (e.g. N_2^+), which does not create electrically active acceptors.

To avoid or to minimize the hydrogen passivation originating from the carrier gas, RWTH Aachen used **nitrogen** instead of hydrogen in a set of experiments. This should reduce possible hydrogen incorporation from the carrier gas. However, with the nitrogen carrier gas, all the main characteristics of the layers depended in the same way on the growth parameters, as when one uses hydrogen carrier gas. This shows that the semiinsulating behavior of the samples could not be avoided by simply exchanging the carrier gas.

When nitrogen is used as a carrier gas, the hydrogen passivation can be explained with collisions and reactions between the plasma activated nitrogen and the metalorganic material which contains hydrogen in its molecules. They will be activated and can be incorporated in the layers. Furthermore, the growth rate of the ZnSe films is reduced, because the diffusion from the gas phase to the substrate surface is slower and the higher temperature gradient above the sample is responsible for a more drastic decrease of the temperature resulting in a smaller region in which the precursor material can be decomposed.

Although the quality of the material grown in nitrogen is comparable to the layers grown in hydrogen, no p-type conductivity was observed. This makes a completely different doping process necessary.

4.3.2 *Doping with nitrogen-containing chemicals*

A different doping process using nitrogen-containing chemicals was investigated. The precursors investigated were as follows: triallylamine ($N(\text{allyl})_3$), trimethylsilylazide (Me_3SiN_3), ethylzincdiisopropylamine ($\text{EtZnN}^i\text{Pr}_2$), bis-ditrimethylsilylamidozinc (Zn-BTM) and ethylbistrimethylsilylamidozinc (EtZnBTM). These precursors have a number of potential advantages:

No nitrogen-hydrogen bonds are present in the molecules. This should minimize hydrogen incorporation in the ZnSe layers.

Precursors decomposition may provide nitrogen in a highly active form.

A preformed [Zn-N] bond should assist the incorporation of nitrogen on the desired Se site in the crystal lattice.

It was found that $N(\text{allyl})_3$, Me_3SiN_3 , and $\text{EtZnN}^i\text{Pr}_2$ were not suitable nitrogen sources, being either too stable or leading to poor layer quality (see Table 3). However, both Zn-BTM and EtZn-BTM did allow the incorporation of significant quantities (ea. 10^{17} cm^{-3}) of nitrogen in ZnSe, as shown by a large (DAP) emission in the low temperature PL spectrum (see Table 3). Unfortunately, the layers did not show p-type conductivity, due either to background doping (halide) or hydrogen passivation from the decomposed metalorganic precursor.

4.3.3 *Growth and Optimization of Quantum-well Structures*

To increase the lifetime of a ZnSe-based optoelectronic device, it is necessary to decrease the strain between the ZnSSe layer and the GaAs substrate. This was successfully achieved by adding Mg to the ZnSSe to obtain lattice-matched ZnMgSSe on GaAs. Initially the precursor combination used was: $\text{Me}_2\text{Zn}(\text{NEt}_3)$, Cp_2Mg , t-BuSH and t-Bu₂Se, but problems of solid pickup led to the use of $(\text{MeCp})_2\text{Mg}$ in place of Cp_2Mg . It was also found that t-BuSH prereacted with the Mg precursor, so that t-Bu₂S was selected as the optimum sulphur source.

High optical and structural quality ZnMgSSe was subsequently grown using $\text{Me}_2\text{Zn}(\text{NEt}_3)/(\text{MeCp})_2\text{Mg}$, t-Bu₂S and t-Bu₂Se, and quantum-size effects were observed in the PL of layers containing quantum wells of different thickness (L_z). The energy of the emitted light was related to L_z^{-2} , as predicted by theory. Furthermore, laser action by optical and electron beam pumping was observed at low thresholds, demonstrating the high quality of these structures.

5. Conclusions

- The optimum precursors for depositing high quality ZnSe/ZnS have been determined and their synthesis and purification routes developed to yield product of the highest possible purity. Handling techniques have been improved to allow the successful scale up of organometallic precursor manufacture, and commercial scale batches (100 - 200 g) of $\text{Me}_2\text{Zn} \cdot \text{NEt}_3$, tBu_2Se , tBuSH , tBu_2S , and $(\text{MeCp})_2\text{Mg}$ can now be prepared with high purity.

A large range of zinc-alkylamide precursors have been synthesised and fully characterized, with $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{EtZnN}(\text{SiMe}_3)_2$ showing most promise as nitrogen-dopant sources.

Most of the unsolved problems at the start of this project were solved during this project.

- Quarternary, ternary and binary layers can be grown with an optimized precursor combination of DTBSe , $\text{DMZn}(\text{TEN})$, DTBS , and $(\text{MeCp})_2\text{Mg}$. The growth temperature could be reduced to increase the electrical quality of the layers, They are not semiinsulating any more due to defect generation at high growth temperatures. Therefore, it was necessary to drastically improve the purity of the precursors. RWTH Aachen has shown that impurities are better incorporated into the layers at low growth temperatures.
- Quantum size effects with several material combinations were demonstrated. An optimized switching sequence to increase the quality of the quantum well interfaces was developed.
Lattice-matched ZnMgSSe material was grown with excellent optical and structural quality. This is necessary to avoid defect generation by strain between the substrate and epilayer. (Defects cause degeneration effects in laser devices.)
- n-type doping was achieved.
Nitrogen could be incorporated in the layers.
Optical and electron beam pumped blue green lasers at room temperature were demonstrated

Only one important challenge remains: so far, the incorporated nitrogen is not electrically active. The compensation mechanisms, like volatility of the dopant, potential fluctuations, complexes including nitrogen and intrinsic defects, hydrogen passivation, and many more are discussed in the literature. Many theories were developed to describe the empirical data.

The problems of compensation, especially related to the MOVPE growth method, have to be solved in the future. Two problems, in particular, should be resolved for MOVPE:

- hydrogen passivation of the p-type conductivity.
- incorporation of nitrogen complexes including that a 'nitrogen species' (meaning that the incorporated nitrogen is electrically de-activated) is incorporated on a wrong site in the crystal.

The problems have to be solved with experiments including different plasma activation (e.g. rf-plasma), different alkylamides, exchange of the carrier gas with a very high purity,

This issue of non-electrically active nitrogen is under investigation at RWTH Aachen and may be solved in the future with additional experiments.

6. Acknowledgments

The partners all thank the Brite-EuRam II programme of the European Commission for providing financial help for this project (project BE-7698-93, contract BRE2-CT93-0586). In addition, the group at Aveiro acknowledges the University of Aveiro and the EC for a fellowship for Mr. Claude Boemare.

7. References

1. R. Gunshore, A. Nurmikko and M. Kobayashi, *Physics World* (March 1992) p. 46.
2. T. Yoko, K. Ueda, K. Morio, K. Yamashita, S. Tanaka, *J. Cryst. Growth* (1991) 107, 659.
3. T. Yoko and S. Tanaka, *J. Cryst. Growth* (1992) 117, 415.
4. K. Akimoto, Miyajima, Y. Mori, *Jap. J. Appl. Phys.* (1989) 28 No. 4, L528.
5. W. Reese et al, *MRS Symposium Proceedings* (1992) 242, 281.
6. W. Reese et al., *J. Electronic Matetia* (1992) 21, 361.

TABLE 1ZINC DIALKYLAMIDES AND RELATED COMPOUNDS SYNTHESISED
AT IMPERIAL COLLEGE

1. *Bis(diethylamido)zinc*
2. *Ethyl(diethylamido)zinc*
3. *Methyl(di-iso-propylamido)zinc*
4. *Ethyl(di-iso-propylamido)zinc*
5. *Bis(di-iso-propylamido)zinc*
6. *Methyl(di-iso-butylamido)zinc*
7. *Ethyl(di-iso-butylamido)zinc*
8. *Bis(di-iso-butylamido)zinc*
9. *Methyl(N,N,N-trimethylpropylenediamido)zinc*
10. *Ethyl(N,N,N-trimethylpropylenediamido)zinc*
11. *bis(N,N,N-trimethylpropylenediamido)zinc*
12. *Methyl(N,N,N-trimethylethylenediamido)zinc*
13. *Ethyl(N,N,N-trimethylethylenediamido)zinc*
14. *preparation of $\text{Me}_4\text{Zn}_6\text{O}_2[\text{NMe}(\text{CH}_2)_3\text{NMe}]_4$*
15. *preparation of $\text{Et}_4\text{Zn}_6\text{O}_2[\text{NMe}(\text{CH}_2)_2\text{NMe}]_4$*
16. *Neopentyl(dimethylamido)zinc*
17. *Neopentyl(diethylamido)zinc*
18. *Neopentyl(di-iso-propylamido)zinc*
19. *Neopentyl(di-iso-butylamido)zinc*
20. *t-Butyl(dimethylamido)zinc*
21. *t-Butyl(diethylamido)zinc*
22. *t-Butyl(di-iso-propylamido)zinc*
23. *t-Butyl(di-iso-butylamido)zinc*
24. *Bis(di(trimethylsilylamido))zinc*
25. *Bis(di(trimethylsilylamido))zinc*
26. *Ethyl(di(trimethylsilylamido))zinc*
27. *Methyl(di(trimethylsilylamido))zinc*

TABLE 2

Se AND S PRECURSORS INVESTIGATED IN THE BLUEMAT PROJECT

Se and S precursor	remarks on T_D	
H ₂ S		toxic gas
DES	$T_D > 480^\circ\text{C}$	
TBT	$T_D \approx 330^\circ\text{C}$	prereactions with (MeCp) ₂ Mg
DTBS	$T_D \approx 330^\circ\text{C}$	high quality of the layers very efficient in comparison to TBT
H ₂ Se	low growth temperature	prereactions, toxic gas
DASe	plasma is needed $T_D > 550^\circ\text{C}$	poor layer quality
DESe	$T_D \approx 480^\circ\text{C}$	layers are semiinsulating
DIPSe	$T_D \approx 440^\circ\text{C}$	small concentration of intrinsic defects
DTBSe	$T_D \approx 330^\circ\text{C}$	layers are conducting

TABLE 3

- NITROGEN-CONTAINING CHEMICAL PRECURSORS INVESTIGATED
IN THE *BLUEMAT* PROJECT

Alkylamide	remarks on VI/II ratio	remarks on T _d	remarks on layer conductivity
ETZ			deteriorated layer structure
Zn-BTM	needs a low VI/II ratio (0.005) for nitrogen incorporation (intensity of DAP emission is comparable with excitonic emission)		N-Zn-N structure might be responsible for compensation of the p-type conductivity, no highly reproducible p-type conductivity was achieved
Et-Zn BTM	needs a low VI/II ratio (0.005) for nitrogen incorporation (intensity of DAP emission is comparable with excitonic emission)	needs a decomposition temperature higher than 340°C for the incorporation of nitrogen	no highly reproducible p-type conductivity was achieved
TAN	needs a low VI/II ratio (0.005) to observe DAP emission, deep level defects are detected		overlap of donor states and conduction band is responsible for n-type conductivity