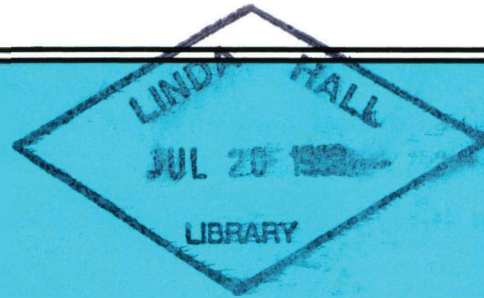


JOURNAL OF **CRYSTAL GROWTH**

VOLUME 204, No. 3, pp. 247-418
JULY II (1999)



EDITORS:

G.B. STRINGFELLOW (Principal Editor),
University of Utah

M. SCHIEBER (Founding Editor),
Hebrew University

R.S. FEIGELSON, Stanford University

D.T.J. HURLE, University of Bristol

R. KERN, Université Aix-Marseille

T. NISHINAGA, University of Tokyo

NOW included in your subscription:
**ELECTRONIC
ACCESS**
www.elsevier.nl/locate/elecacc

CO-FOUNDERS: N. CABRERA, B. CHALMERS, F.C. FRANK
FORMER ADVISOR: R.A. LAUDISE†

North-Holland

<http://www.elsevier.nl/locate/jcrysgr>

Journal of Crystal Growth

EDITORIAL BOARD

G.B. STRINGFELLOW (Principal Editor)
College of Eng., Univ. Utah
1495 East 100 South, Room 214
Salt Lake City, UT 84112-1109, USA
Fax: +1 801 581 8692
E-mail: stringfellow@eng.utah.edu

M. SCHIEBER (Founding Editor)
The Fredy and Nadine Herrmann
Graduate School of Appl. Sci.
Hebrew University, Jerusalem 91904, Israel
Fax: +972 2 566 3878
E-mail: schieber@vms.huji.ac.il

R.S. FEIGELSON
Ctr. Materials Res., Press Warehouse
Stanford University
Stanford, CA 94305-4045, USA
Fax: +1 650 723 3752/3044
E-mail: feigel@soe.stanford.edu

D.T.J. HURLE
H.H. Wills Phys. Lab.
University of Bristol
Tyndall Avenue
Bristol BS8 1TL, UK
E-mail: donhurle@usa.net

R. KERN
CRM2, CNRS, Campus Luminy, Case 913
F-13288 Marseille Cedex 9, France
Fax: +33 4 91 418 916
E-mail: kern@crmc2.univ-mrs.fr

T. NISHINAGA
Dept. Electron. Eng., University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan
Fax: +81 3 5841 6068
E-mail: tatau@ee.t.u-tokyo.ac.jp

ASSOCIATE EDITORS

C.R. ABERNATHY (*Chemical Beam Epitaxy, III-Nitrides, Novel Dielectrics*)
K.W. BENZ (*Microgravity, Electronic Materials*)
N.E. CHAYEN (*Crystallization of Biological Macromolecules*)
A.A. CHERNOV (*Kinetics of Crystallization, Protein Crystallization*)
A.Y. CHO (*Molecular Beam Epitaxy*)
S.R. CORIELL (*Theory*)
J.J. DERBY (*Computational Models*)
M.E. GLICKSMAN (*Solidification*)
M.S. GOORSKY (*XRD Characterization, Epitaxy for Devices*)
T. HIBIYA (*Oxides, Melt Thermophysical Properties, Microgravity*)
S. HIYAMIZU (*Molecular Beam Epitaxy*)
R. JAMES (*II-VI Semiconductors, Radiation Sensors*)
T.F. KUECH (*Thin Films and Electronic and Optical Devices*)

A. McPHERSON (*Protein Growth*)
P.A. MORRIS HOTSENPILLER (*Electrooptical Crystals, Oxide Thin Films, Book Reviews*)
J.B. MULLIN (*Semiconductors*)
K. NAKAJIMA (*Liquid and Vapor Phase Epitaxy*)
H. OHNO (*Epitaxy*)
K. PLOOG (*Molecular Beam Epitaxy*)
R.W. ROUSSEAU (*Solution Growth, Industrial Crystallization*)
K. SATO (*Biocrystallization and Organic Crystals*)
L.F. SCHNEEMEYER (*Superconductivity, Oxides, Novel Materials, Priority Communications*)
D.W. SHAW (*Semiconductors, Epitaxy, Devices*)
M. UWAHA (*Growth Kinetics*)
A.F. WITT (*Semiconductor Crystals*)
A. ZANGWILL (*Theory (Epitaxy)*)

Scope of the journal

Experimental and theoretical contributions are invited in the following fields: Theory of nucleation and growth, molecular kinetics and transport phenomena, crystallization in viscous media such as polymers and glasses. Crystal growth of metals, minerals, semiconductors, magnetics, inorganic, organic and biological substances in bulk or as thin films. Apparatus, instrumentation and techniques for crystal growth, and purification methods. Characterization of single crystals by physical and chemical methods.

Abstracted/indexed in

Aluminium Industry Abstracts; Chemical Abstracts; Current Contents: Physical, Chemical and Earth Sciences; EI Compendex Plus; Engineered Materials Abstracts; Engineering Index; INSPEC; Metals Abstracts.

Publication information

Journal of Crystal Growth (ISSN 0022-0248). For 1999, volumes 195–207 are scheduled for publication. Subscription prices are available upon request from the Publisher or from the Regional Sales Office nearest you or from this journal's website (<http://www.elsevier.nl/locate/jcrysgro>). Further information on this journal and other Elsevier Science products is available through Elsevier's website (<http://www.elsevier.nl>). Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by standard mail (surface within Europe, air delivery outside Europe). Priority rates are available upon request. Claims for missing issues should be made within six months of the date of dispatch.

Orders, claims, and product enquiries

Please contact the Customer Support Department at the Regional Sales Office nearest you:

New York: Elsevier Science, P.O. Box 945, New York, NY 10159-0945, USA; tel.: +1 212 633 3730 [toll free number for North American customers: 1-888-4ES-INFO (437-4636)]; fax: +1 212 633 3680; e-mail: usinfo-f@elsevier.com.

Amsterdam: Elsevier Science, P.O. Box 211, 1000 AE Amsterdam, The Netherlands; tel.: +31 20 485 3757; fax: +31 20 485 3432; e-mail: nlinfo-f@elsevier.nl.

Tokyo: Elsevier Science, 9-15 Higashi-Azabu 1-chome, Minato-ku, Tokyo 106-0044, Japan; tel.: +81 3 5561 5033; fax: +81 3 5561 5047; e-mail: info@elsevier.co.jp.

Singapore: Elsevier Science, No. 1 Temasek Avenue, #17-1 Millenia Tower, Singapore 039192; tel.: +65 434 3727; fax: +65 337 2230; e-mail: asiainfo@elsevier.com.sg.

Rio de Janeiro: Elsevier Science, Rua Sete de Setembro 111/16 Andar, 20050-002 Centro, Rio de Janeiro – RJ, Brazil; tel.: +55 21 509 5340; fax: +55 21 507 1991; e-mail: elsevier@campus.com.br. [Note: (Latin America): for orders, claims and help desk information, please contact the Regional Sales Office in New York as listed above.]

Advertising information

Advertising orders and enquiries can be sent to:

USA, Canada and South America: Mr. Tino de Carlo, The Advertising Department, Elsevier Science Inc., 655 Avenue of the Americas, New York, NY 10010-5107, USA; tel.: +1 212 633 3815; fax: +1 212 633 3820; e-mail: t.decarlo@elsevier.com.

Japan: The Advertising Department, Elsevier Science K.K., 9-15 Higashi-Azabu 1-chome, Minato-ku, Tokyo 106-0044, Japan; tel.: +81 3 5561 5033; fax: +81 3 5561 5047.

Europe and ROW: Rachel Gresle-Farthing, The Advertising Department, Elsevier Science Ltd., The Boulevard, Langford Lane, Kidlington, Oxford OX5 1GB, UK; tel.: +44 1865 843565; fax: +44 1865 843976; e-mail: r.gresle-farthing@elsevier.co.uk.

USA mailing notice: Journal of Crystal Growth (ISSN 0022-0248) is published semimonthly by Elsevier Science B.V. (P.O. Box 211, 1000 AE Amsterdam, The Netherlands). Annual subscription price in the USA is US\$ 7545 (valid in North, Central and South America), including air speed delivery. Periodicals postage rate paid at Jamaica, NY 11431, USA.
USA Postmaster: Send address changes to Journal of Crystal Growth, Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003, USA.
Airfreight and mailing in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003, USA.

Ⓢ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper)

North-Holland, an imprint of Elsevier Science

PRINTED IN THE NETHERLANDS



EDITORIAL BOARD

G.B. STRINGFELLOW (Principal Editor)
College of Eng., Univ. Utah
1495 East 100 South, Room 214
Salt Lake City, UT 84112-1109, USA
Fax: +1 801 581 8692
E-mail: stringfellow@eng.utah.edu

M. SCHIEBER (Founding Editor)
The Fredy and Nadine Herrmann
Graduate School of Appl. Sci.
Hebrew University, Jerusalem 91904, Israel
Fax: +972 2 566 3878
E-mail: schieber@vms.huji.ac.il

R.S. FEIGELSON
Ctr. Materials Res., Press Warehouse
Stanford University
Stanford, CA 94305-4045, USA
Fax: +1 650 723 3752/3044
E-mail: feigel@soe.stanford.edu

D.T.J. HURLE
H.H. Wills Phys. Lab.
University of Bristol
Tyndall Avenue
Bristol BS8 1TL, UK
E-mail: donhurle@usa.net

R. KERN
CRM2, CNRS, Campus Luminy, Case 913
F-13288 Marseille Cedex 9, France
Fax: +33 4 91 418 916
E-mail: kern@crmc2.univ-mrs.fr

T. NISHINAGA
Dept. Electron. Eng., University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan
Fax: +81 3 5841 6068
E-mail: tatau@ee.t.u-tokyo.ac.jp

ASSOCIATE EDITORS

C.R. ABERNATHY (*Chemical Beam Epitaxy, III-Nitrides, Novel Dielectrics*)
Dept. Mater. Sci. Eng., Univ. Florida
Rhines Hall, Gainesville, FL 32606, USA
Fax: +1 352 846 1182
E-mail: caber@mse.ufl.edu

K.W. BENZ (*Microgravity, Electronic Materials*)
Kristallographisches Inst., Universität
Hebelstr. 25, D-79104 Freiburg, Germany
Fax: +49 761 203 4369
E-mail: benz@ruf.uni-freiburg.de

N.E. CHAYEN (*Crystallization of Biological Macromolecules*)
Biophysics Section, Physics Dept.
Imperial College, London SW7 2BZ, UK
Fax: +44 171 589 0191
E-mail: n.chayen@ic.ac.uk

A.A. CHERNOV (*Kinetics of Crystallization, Protein Crystallization*)
Inst. Crystallography, Acad. of Sciences
Leninskii Prosp., Moscow 117333
Russian Fed.
Fax: +7 095 135 1011
Univ. Space Res. Assoc., 4950 Corp. Dr.
Ste. 100, Huntsville, AL 35805, USA
Fax: +1 205 544 8762
E-mail: alex.chernov@msfc.nasa.gov

A.Y. CHO (*Molecular Beam Epitaxy*)
Lucent Technol., Room 6H-422
600 Mountain Ave.
Murray Hill, NJ 07974-0636, USA
Fax: +1 908 582 2043
E-mail: ayo@lucent.com

S.R. CORIELL (*Theory*)
A153 Mater.
Nat. Inst. of Standards & Technol.
Gaithersburgh, MD 20899-0001, USA
Fax: +1 301 975 4553
E-mail: coriell@nist.gov

J.J. DERBY (*Computational Models*)
Dept. Chem. Eng. & Mater. Sci.
Univ. Minnesota, 151 Amundson Hall
421 Washington Ave. S.E.
Minneapolis, MN 55455-0132, USA
Fax: +1 612 626 7246
E-mail: derby@maroon.tc.umn.edu

M.E. GLICKSMAN (*Solidification*)
School of Eng., Mater. Eng. Dept.
Rensselaer Polytechnic Inst.
Troy, NY 12180-3590, USA
Fax: +1 518 276 2198
E-mail: glickm@rpi.edu

M.S. GOORSKY (*XRD Characterization, Epitaxy for Devices*)
Dept. Mater. Sci. Eng., Univ. California
Los Angeles, CA 90095-1595, USA
Fax: +1 310 206 7353
E-mail: goorsky@seas.ucla.edu

T. HIBIYA (*Oxides, Melt Thermophysical Properties, Microgravity*)
Fundamental Res. Labs., NEC Corp.
34, Miyukigaoka, Tsukuba 305, Japan
Fax: +81 298 566 136
E-mail: hibiya@frl.nec.co.jp

S. HIYAMIZU (*Molecular Beam Epitaxy*)
Dept. Phys. Sci., Graduate School Eng. Sci.
Osaka Univ., Toyonaka, Osaka 560, Japan
Fax: +81 6 845 4632
E-mail: hiyamizu@mp.es.osaka-u.ac.jp

R. JAMES (*II-VI Semiconductors, Radiation Sensors*)
Sandia National Labs., MS 9405
7011 East Ave., Livermore, CA 94550, USA
Fax: +1 925 294 3870
E-mail: rbjames@sandia.gov

T.F. KUECH (*Thin Films and Electronic and Optical Devices*)
Dept. Chem. Eng.
Univ. Wisconsin-Madison
Madison, WI 53706, USA
Fax: +1 608 265 3782
E-mail: kuech@engr.wisc.edu

A. McPHERSON (*Protein Growth*)
Dept. Mol. Biol. & Biochem.
Univ. California
Irvine, CA 92697-3900, USA
Fax: +1 949 824 1954
E-mail: amcphe@uci.edu

P.A. MORRIS HOTSENPILLER (*Electrooptical Crystals, Oxide Thin Films, Book Reviews*)
DuPont Central Res. & Devel., Exp. Station
P.O. Box 80356
Wilmington, DE 19880-0356, USA
Fax: +1 302 695 1664; E-mail: patricia.a.morris-hotsenpiller@usa.dupont.com

J.B. MULLIN (*Semiconductors*)
EMC, "The Hoo", Brockhill Road
West Malvern, Worcs. WR14 4DL, UK
Fax: +44 1684 575 591
E-mail: brian.mullin@btinternet.com

K. NAKAJIMA (*Liquid and Vapor Phase Epitaxy*)
Inst. Mater. Res., Tohoku Univ.
Katahira 2-1-1, Sendai 980-8577, Japan
Fax: +81 22 215 2011
E-mail: nakajima@imr.tohoku.ac.jp

H. OHNO (*Epitaxy*)
Research Inst. of Electrical Commun.
Tohoku Univ., Sendai 980-8577, Japan
Fax: +81 22 217 5553
E-mail: ohno@rice.tohoku.ac.jp

K. PLOOG (*Molecular Beam Epitaxy*)
Paul-Drude-Inst. für Festkörperelektronik
Hausvogteiplatz 5-7
D-10117 Berlin, Germany
Fax: +49 30 203 77201
E-mail: ploog@pdi-berlin.de

R.W. ROUSSEAU (*Solution Growth, Industrial Crystallization*)
School of Chem. Eng.
Georgia Inst. of Technol.
Atlanta, GA 30332-0100, USA
Fax: +1 404 894 2866
E-mail: ronald.rousseau@che.gatech.edu

K. SATO (*Biocrystallization and Organic Crystals*)
Fac. Appl. Biol. Sci., Hiroshima Univ.
Higashi-Hiroshima 724, Japan
Fax: +81 824 227 062
E-mail: kyosato@ipc.hiroshima-u.ac.jp

L.F. SCHNEEMEYER (*Superconductivity, Oxides, Novel Materials, Priority Communications*)
Room 1A-363, AT&T Bell Labs.
Murray Hill, NJ 07974-2070, USA
Fax: +1 908 582 2521
E-mail: schneemeyer@bell-labs.com

D.W. SHAW (*Semiconductors, Epitaxy, Devices*)
Univ. Texas, 10009 Apple Creek Dr.
Dallas, TX 75243, USA
Fax: +1 972 234 2648
E-mail: dns@worldnet.att.net

M. UWABA (*Growth Kinetics*)
Dept. Physics, Nagoya Univ.
Furo-cho, Chikusa-ku, Nagoya 464-8602
Japan
Fax: +81 52 789 2928
E-mail: uwaba@phys.nagoya-u.ac.jp

A.F. WITT (*Semiconductor Crystals*)
Dept. of Metall. & Mater. Sci.
Massachusetts Inst. of Technol.
Cambridge, MA 02139, USA
Fax: +1 617 253 5827
E-mail: afwitt@mit.edu

A. ZANGWILL (*Theory (Epitaxy)*)
School of Physics, Georgia Inst. of Technol.
Atlanta, GA 30332, USA
Fax: +1 404 894 9958
E-mail: andrew.zangwill@physics.gatech.edu

© 1999 Elsevier Science B.V. All rights reserved

This journal and the individual contributions contained in it are protected under copyright by Elsevier Science B.V., and the following terms and conditions apply to their use:

Photocopying

Single photocopies of single articles may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier Science Rights & Permissions Department, P.O. Box 800, Oxford OX5 1DX, UK; tel.: +44 1865 843830, fax: +44 1865 853333, e-mail: permissions@elsevier.co.uk. You may also contact Rights & Permissions directly through Elsevier's home page (<http://www.elsevier.nl>), selecting first 'Customer Support', then 'General Information', then 'Permissions Query Form'.

In the USA, users may clear permissions and make payments through the Copyright Clearing Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; tel.: +1 978 7508400, fax: +1 978 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; tel.: +44 171 631 5555, fax: +44 171 631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative works

Subscribers may reproduce tables of contents or prepare lists of articles including abstracts for internal circulation within their institutions. Permission of the Publisher is required for resale or distribution outside the institution.

Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic storage or usage

Permission of the Publisher is required to store or use electronically any material contained in this journal, including any article or part of an article.

Except as outlined above, no part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.

Address permissions requests to: Elsevier Science Rights & Permissions Department, at the mail, fax and e-mail addresses noted above.

Notice

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made. Although all advertising material is expected to conform to ethical (medical) standards, inclusion in this publication does not constitute a guarantee or endorsement of the quality of such product or of the claims made of it by its manufacturer.

⊙ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper)

PRINTED IN THE NETHERLANDS



ELSEVIER

Journal of Crystal Growth 204 (1999) 256–262

JOURNAL OF
**CRYSTAL
GROWTH**

www.elsevier.nl/locate/jcrysgro

Metal organic vapour-phase epitaxy (MOVPE) growth of InP and InGaAs using tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) in N₂ ambient

D. Keiper*, R. Westphalen, G. Landgren

Department of Electronics, Royal Institute of Technology (KTH), Electrum 229, S-164 40 Kista, Sweden

Received 12 June 1998; accepted 11 April 1999

Communicated by J.B. Mullin

Abstract

We have investigated the growth of InP and InGaAs/InP using TBA and TBP in N₂ ambient. This process eliminates both the explosive H₂ and the toxic hydrides as precursors. General growth aspects are reported and the process window for defect free growth is determined to be $T_{\text{growth}} > 660^\circ$ and a minimal V/III ratio ≤ 20 at 100 mbar. The uniformity improves and the electrical characteristics are comparable or better than those of the standard MOVPE process. Broad area bulk (Q(1.57 μm)) lasers reveal current densities below 2 kA/cm². © 1999 Elsevier Science B.V. All rights reserved.

PACS: A.81.15.H; B.05.10.D; B.25.20.D; A.64.80.E

Keywords: TBA; TBP; Alternative V-sources; MOVPE; MOCVD; Nitrogen

1. Introduction

In general, the metal organic vapour-phase epitaxy (MOVPE) process uses the toxic hydrides PH₃ and AsH₃ as group V-precursors. For safety reasons therefore many alternative, less toxic group V-sources have been investigated. Devices made from structures grown with the alternative group V-sources tertiarybutylarsine (TBA) and tertiarybutylphosphine (TBP) exhibit state of the art performance see e.g., Ref. [1]. Also other alternative group V-precursors like diethyltertiarybutylarsine

(DEtBA) and ditertiarybutylphosphine (DitBuPH) reveal the ability to grow state of the art devices [2]. The compositional uniformity of quaternary material is significantly enhanced using TBA/TBP in vertical as well as horizontal reactors with H₂ as carrier gas [3].

Up to now point of use purified H₂ is the generally accepted carrier gas for MOVPE. For some years now efficient N₂ purifiers are also available. The electrical and optical characteristics of MOVPE-layers grown in N₂ ambient have been investigated and they show improvements in material quality [4,5]. Furthermore, a better wafer uniformity was obtained [6].

The combination of inert N₂ and TBA/TBP was used by Hsu et al. [7] to grow GaAs-based HBT structures, which show maximum oscillation

* Corresponding author. Tel.: +46-8-752-1157; fax: +46-8-752-1240.

E-mail address: keiper@ele.kth.se (D. Keiper)

frequencies ($f_{\max}$) of up to 120 GHz. Furthermore, Zimmermann et al. [8] compared the use of H_2 or N_2 as carrier gas for the selective area growth (SAG) of InP-based structures using TBA and TBP as group-V sources. They performed their experiments on InP(0 0 1) substrates, patterned with SiN_x and cleaned/etched before growth. Use of N_2 as carrier gas means an increase in safety and gives an additional parameter to control the gas-phase diffusion of the SAG process.

In contrast to Zimmermann et al. [8], we will report in the following on the combination of N_2 and TBA/TBP for the planar growth on unpatterned InP in a commercial MOVPE system. This would provide an inherently “safe process” for MOVPE of III–V materials and in addition has the potential for increased wafer uniformity.

2. Experimental procedure

The growth of the InP and InGaAs layers was carried out in an AIXTRON 200/4 ($3 \times 2''$) low-pressure MOVPE horizontal reactor. The carrier gas was SAES Getter purified nitrogen. The precursors were TBA, TBP, TMIn, and TMGa. H_2 was always used for the MO-source lines. Thus the actual nitrogen content in the reactor was about 90%. The partial pressures were calculated with literature data [9] and the assumption of a linear dependence between the partial pressure and the source flow rate. The gas velocity was kept constant at 0.5 m/s and the growth parameters were $P_{\text{tot}} = 50$ mbar and $Q_{\text{tot}} = 8$ slm total flow or $P_{\text{tot}} = 100$ mbar and $Q_{\text{tot}} = 15$ slm. The growth temperature and the V/III ratio were varied in the range of 580–700°C and 5–75, respectively.

The growth rate was determined by weighing the typically 300 nm thick InGaAs- and InP-layers, with an estimated relative measurement error of $\pm 4\%$. InGaAs was grown at approximately 0.18 nm/s, whereas for InP approximately 0.2 nm/s was applied, except for the 2 μm thick bulk layer for Hall measurement where 0.3 nm/s was used for InP. The composition was measured by high-resolution X-ray diffraction (HRXRD). The majority of the samples were grown on epi-ready InP:S substrates, which were nominally oriented in (0 0 1)

with an error of less than $\pm 0.1^\circ$. Before growth, the wafers were annealed in PH_3 for 5 min at growth temperature, but at least at 610°C. Under these conditions, a defect-free surface for InP is obtained grown with PH_3 in N_2 at 610°C. An approximately 150 nm thick InP buffer layer, utilising PH_3 in N_2 , was grown at 610°C or higher temperatures for the InGaAs layers. No extended attempt to optimise the wafer treatment procedure before growth, e.g. through high-temperature annealing steps, was done. The surface characteristics were evaluated by Nomarski phase-contrast optical microscopy. The carrier concentration and mobility of the nominally undoped 2 μm thick layers deposited on InP:Fe substrates, which were oriented in (0 0 1) $\pm 0.3^\circ$, was obtained from Hall measurements with van de Pauw geometry and a magnetic field of 4 kG.

3. Results and discussion

The growth rate depends, as expected, on the partial pressure of the MO's, the gas velocity and the total pressure [10]. However, it is independent on the V/III ratio within the measurement error of $\pm 4\%$ (e.g. InP, 610°C, V/III = 5–75). This is an indication of very low parasitic gas-phase reactions in contrast to the PH_3 /TMIn case in H_2 [11]. Furthermore, Chui et al. [12] have reported a 30% growth rate decrease by changing the V/III ratio from 5 to 72 for GaAs using TBA in H_2 . They explained this effect with the surface blocking by the TBA species. The influence of the growth temperature on the growth rate is shown for InP in Fig. 1. From 580 to 700°C the growth rate increases by 10%, which is typical for the diffusion limited growth.

The surface morphology for InP and InGaAs is shown in Figs. 2 and 3, respectively. The defect type and density varies primarily with growth temperature but also with V/III ratio. The different defect types are defined in the Appendix. Fig. 2 demonstrates that InP can be grown defect free only for temperatures higher than 660°C and appropriate V/III ratios (for $P_{\text{tot}} = 50$ mbar at least around 40). Similarly, the defect-free growth of InGaAs is established for growth temperatures higher than

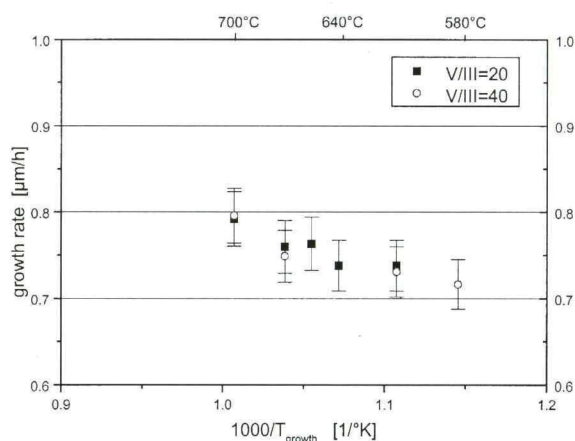


Fig. 1. Growth rate as a function of the inverse growth temperature for InP at different V/III ratios; with $\text{TMIIn} = 9 \times 10^{-5} \text{ mol/min}$, $P_{\text{tot}} = 50 \text{ mbar}$, $Q_{\text{tot}} = 8 \text{ slm}$. The growth rate is 10% higher at 700°C compared to 600°C but is independent on the V/III ratio.

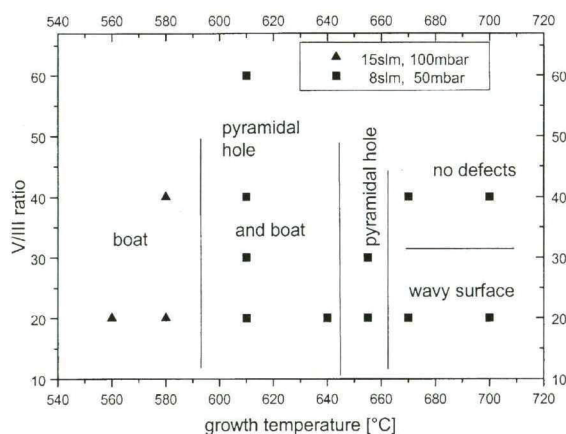


Fig. 2. Defect type distribution for InP grown at different growth temperatures and V/III ratios; with $\text{TMIIn} = 9 \times 10^{-5} \text{ mol/min}$, $P_{\text{tot}} = 50 \text{ mbar}$, $Q_{\text{tot}} = 8 \text{ slm}$. Defect free growth is obtained only for growth temperatures higher than 660°C with a V/III ratio ≥ 40 .

660°C and V/III ratios of at least 10 for 50 mbar as shown in Fig. 3.

Thus only appropriate V/III ratios (40 for InP and 10 for InGaAs at 50 mbar) and temperatures higher than 660°C result in smooth surfaces. These growth conditions are quite similar to our standard process utilising $\text{AsH}_3/\text{PH}_3/\text{H}_2$ at 680°C [13].

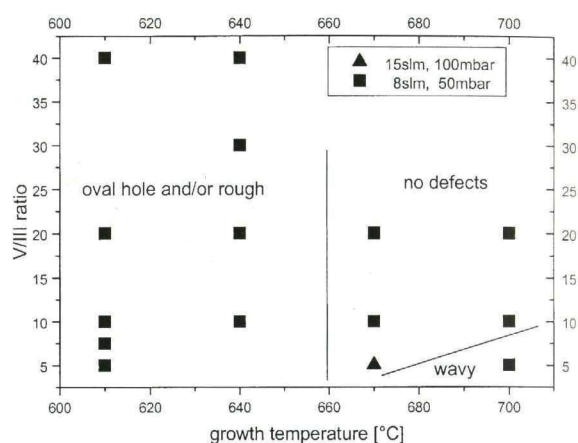


Fig. 3. Defect type distribution at different V/III ratios and growth temperatures for InGaAs; with $\text{TMIIn} = 4.5 \times 10^{-5} \text{ mol/min}$, $\text{TMGa} = 2.5 \times 10^{-5} \text{ mol/min}$, $P_{\text{tot}} = 50 \text{ mbar}$, $Q_{\text{tot}} = 8 \text{ slm}$. Defect free growth is obtained only for growth temperatures higher than 660°C with a V/III ratio ≥ 10 . By increasing the growth pressure to $P_{\text{tot}} = 100 \text{ mbar}$ with $Q_{\text{tot}} = 15 \text{ slm}$, the V/III ratio can be reduced to 5, to establish a defect free 300 nm thick InGaAs layer. But for a 2 μm thick InGaAs layer the surface gets rough for a V/III ratio of lower than 10.

These relatively high growth temperatures for the alternative group V-sources are in contrast to the growth in H_2 , where usually temperatures well below 650°C are used [2,14–16]. A possible explanation for this, is suppressed desorption of the butyl groups from the surface in N_2 . The reduction of the wavy surface by increasing the V/III ratio and thus reducing the surface mobility is in correspondence with previous observations [17]. Furthermore, the wavy surface can be suppressed by a higher total pressure (Fig. 3). This reduces the surface mobility first by the higher pressure itself and second because increasing the pressure from 50 to 100 mbar results in less desorption of the group V-material, thus inducing a higher effective V/III ratio on the surface. This means that at higher total pressures the input V/III ratio can be reduced without degrading the material surface.

In contrast to this observation is the report of Hsu et al. [7]. They reported the growth of GaInP/GaAs in a horizontal MOVPE reactor utilising growth temperatures lower than 660°C using TBA/TBP in N_2 . The reason for this discrepancy is

unclear but the higher bond strength of the GaAs-based material and thus an other surface chemistry could effect the defect formation. Furthermore, their use of CCl_4 as carbon precursor results in reactive chlorine which etch the surface during growth and thus can suppress the defect formation. Zimmermann et al. [8] addressed the SAG growth with TBA/TBP/ N_2 at $T_g = 610^\circ\text{C}$ without observing defects in the unmasked areas. This growth temperature is definitely lower than our observed growth window of $T_g \geq 660^\circ\text{C}$ and cannot be explained by differences in the temperature measurement.

The electrical characteristics of InP and InGaAs were evaluated on 2 μm thick layers grown without a buffer on InP:Fe substrates at 680°C , $P_{\text{tot}} = 100$ mbar and $Q_{\text{tot}} = 15$ slm. The InP V/III ratio was 20 and for InGaAs 10. All samples were defect free, as defined in the Appendix. The carrier concentrations and mobilities are shown in Table 1 calculated for the nominal layer thickness. Table 1 shows the results for InP and InGaAs, and for comparison the typical electrical characteristics for our standard process with $\text{PH}_3/\text{AsH}_3/\text{H}_2$ grown with the same growth parameters.

For InP the background doping was 5×10^{14} (3×10^{14}) cm^{-3} at 300 K (77 K) and the mobility 3400 (66 000) V s/cm^2 . For InGaAs we determined a carrier-concentration of 2×10^{14} (9×10^{13}) cm^{-3} and a mobility of 9800 (50 000) V s/cm^2 . Compared to the conventional process with PH_3/AsH_3 under H_2 (V/III ratio ≈ 100), the background dop-

ing level is reduced by a factor of approximately 5 for InP and 10 for InGaAs. No correction for the depletion layers was included in the Hall data calculation. Estimating the depletion layer widths, the background doping increases and the background doping difference is reduced by about a factor of 2. In conclusion, the use of the TBA/TBP/ N_2 process instead of the $\text{PH}_3/\text{AsH}_3/\text{H}_2$ leads to an improvement in all electrical data, except for the 77 K mobility of InGaAs which we attribute to a lower conductive layer at the InGaAs/InP:Fe interface following a simple two conducting layer model for Hall measurements [18].

The relaxed mismatch variation of InGaAs over 40 mm of a 50 mm diameter wafer was reduced to less than 80 ppm as measured by HRXRD, as opposed to 150 ppm in the H_2 case. Furthermore the uniformity for an InGaAs/InP MQW structure with 8 nm thick wells and 8 nm thick barriers also improves [6], and the area within a certain specified wavelength doubles compared to the H_2 case as shown in Fig. 4. Apart from the improved InGaAs composition uniformity an improved thickness uniformity contributes to this MQW result. Further uniformity aspects have been discussed in more detail in Ref. [19].

To test the utility of this process with TBA/TBP/ N_2 , broad stripe DH-laser diodes with 200 nm thick 1.57 μm quaternary material were processed. The threshold current density for $900 \times 50 \mu\text{m}^2$ stripe lasers is 1.9 kA/cm^2 , which was comparable to the $\text{PH}_3/\text{AsH}_3/\text{H}_2$ process [2].

Table 1

Hall-measurement data for InP and InGaAs are calculated without considering a depletion layer. (The growth was carried out at 680°C and 100 mbar with a V/III ratio of 20 and $\text{TMin} = 1.3 \times 10^{-4}$ mol/min for InP, utilising TBP/ N_2 , whereas for InGaAs a V/III ratio of 10, $\text{TMin} = 4.5 \times 10^{-5}$ mol/min and $\text{TMGa} = 2.6 \times 10^{-5}$ mol/min, was used with TBA/ N_2 . For the $\text{PH}_3/\text{AsH}_3/\text{H}_2$ process, a V/III ≈ 100 was employed. The background doping is reduced for the TBA/TBP/ N_2 process whereas the mobilities are the same for both processes)

MOVPE-process	Temp. (K)	InP		InGaAs	
		(cm^{-3})	(V s/cm^2)	(cm^{-3})	(V s/cm^2)
TBA/TBP/ N_2	300	5.0×10^{14}	3400	2.0×10^{14}	9800
	77	3.0×10^{14}	66 000	9.0×10^{13}	50 000
$\text{AsH}_3/\text{PH}_3/\text{H}_2$	300	3.0×10^{15}	3000	3.0×10^{15}	9000
	77	1.0×10^{15}	60 000	1.0×10^{15}	62 000

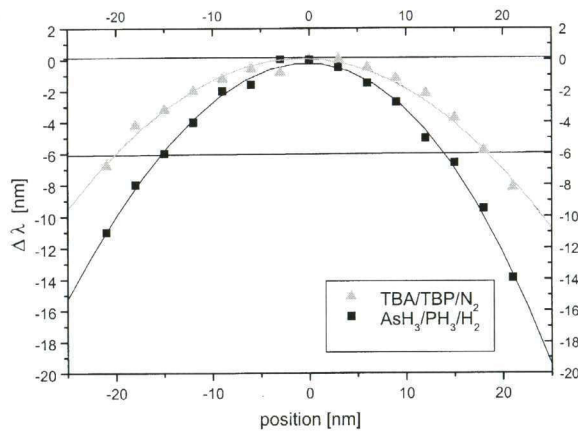


Fig. 4. The absolute wavelength deviation ($\Delta\lambda$) of $PL_{\max}$ for a MQW structure is shown for 40 mm of a 2" wafer grown with TBA/TBP/ N_2 and $AsH_3/PH_3/H_2$. The MQW consists of 20×8 nm thick InGaAs wells and 8 nm thick InP barriers. The two lines at -6 and 0 nm indicate a hypothetical useful wafer area within a tolerance of ± 3 nm. Thus, the useful wafer area doubles for the TBA/TBP/ N_2 process.

4. Conclusions

It is shown that the defect-free deposition of InP and InGaAs/InP via MOVPE is possible using TBP and TBA in N_2 ambient. The growth window for this process is evaluated and the growth temperature for defect-free deposition is higher than 660°C and the V/III ratio is roughly 10–20% of the standard MOVPE process. The electrical properties are comparable or better than with the standard process (PH_3 , AsH_3 in H_2). With the new process it is possible to grow good quality DH-lasers. The uniformity across the wafer improves significantly with respect to composition as well as thickness.

Acknowledgements

This report was financed by the Swedish Foundation for Strategic Research (SSF).

Appendix A. Defect types

The different kinds of defects, which were observed during this investigation, are defined in the

following. Figs. 5a–c show optical microscope pictures of some defects. The defect dimensions can be obtained from these pictures and were cross checked by AFM investigations.

An *oval hole defect* (Fig. 5a) has an oval shape in the dimension of up to $8\ \mu\text{m}$ long and $3\ \mu\text{m}$ wide. The plateau in the middle of the defect is about 30 nm lower than the wafer surface and has steep borders. In the middle of these plateaus usually a small swelling is situated with a height of 3 nm relative to the plateau-ground. The longer dimension of the ovals lies in the $[0\ \bar{1}\ 1]$ direction. The dimensions of the defects on a wafer vary. This kind of defect seems to be the same as the type IV defect in Ref. [20].

A *boat defect* (Fig. 5b) has also an oval shape with the dimensions of up to $25\ \mu\text{m}$ long and $6\ \mu\text{m}$ wide. The top of the defects is about 100 nm higher than the wafer surface and the side planes show crystallographic planes. The orientation of the long direction is in $[0\ 1\ \bar{1}]$ and thus perpendicular to the oval hole defect. The defect sizes differ on the wafer.

A *pyramidal hole defect* (Fig. 5c) has the shape of an inverted pyramid with the dimensions of $13 \times 13\ \mu\text{m}^2$. The “top” of these defects is about 35 nm lower than the wafer surface and the sides are oriented in $\langle 0\ 1\ 1 \rangle$. The sizes of the defects are the same on a wafer. Furthermore, this type is usually not statistically distributed over the wafer but lined up, especially in the $[0\ \bar{1}\ \bar{1}]$ direction close to the big flat.

A *wave defect* shows a regular, wave like surface modulation with an amplitude of 2.5 nm and a “period” of $3\ \mu\text{m}$. It can be reduced with higher V/III ratio or lower growth temperature [17].

The surface is called *rough*, if the amount of defects is so large that no separate defect type can be detected with respect to the upper definitions. Thus, the amount of defects is so large that they interfere/collide with each other.

A wafer is called *defect free* if the wafer has no wave-defects, is not rough and has less defects than $15/\text{cm}^2$ of the above or other types.

Whether a defect is caused by the substrate or by the growth conditions is difficult to say, because both these effects cannot be separated. But if the size of the observed defects is the same over

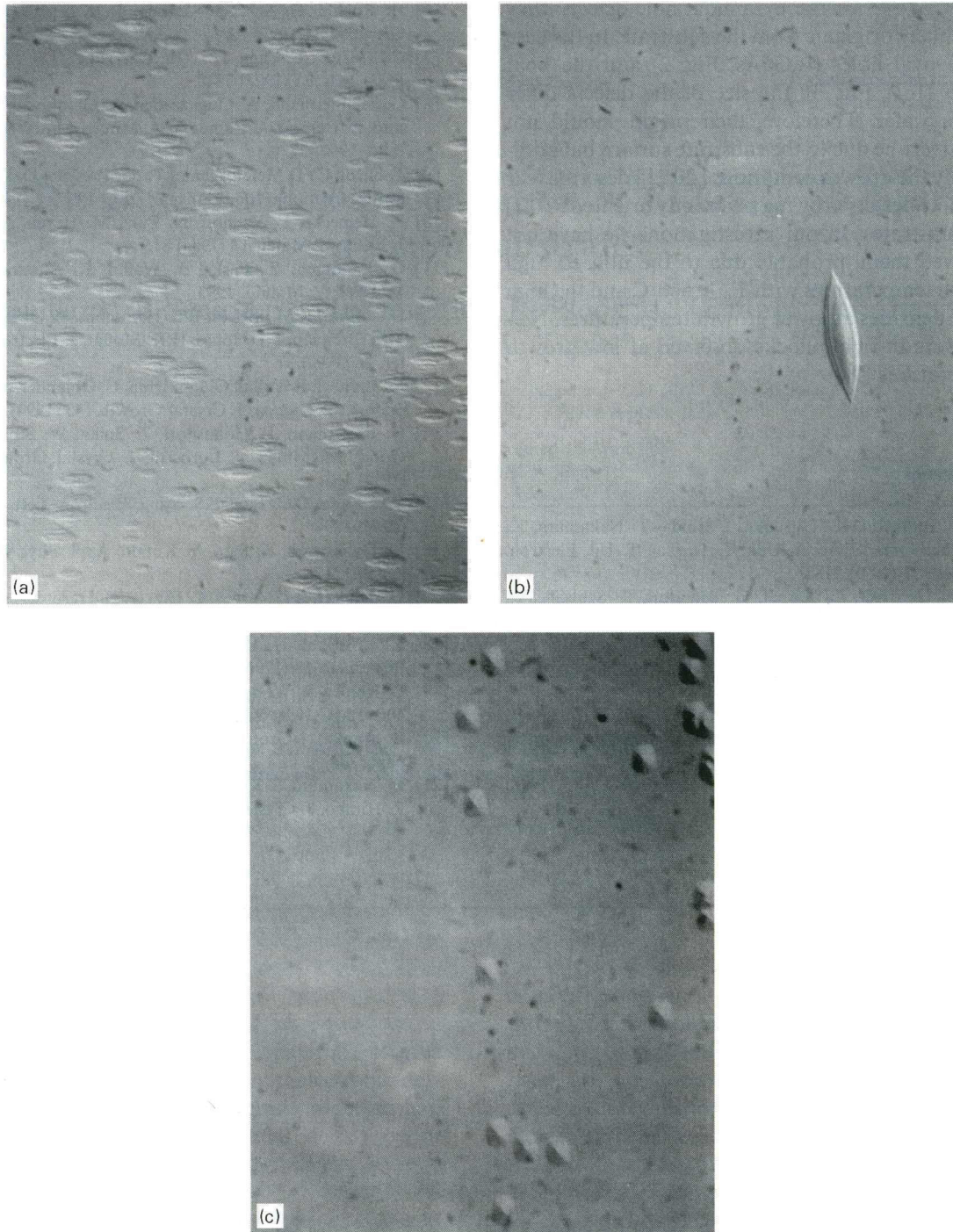


Fig. 5. Optical microscope photo of: (a) oval hole defects with a magnification of $1000\times$; (b) a boat defect with a magnification of $1000\times$; (c) pyramid hole defects with a magnification of $400\times$.

the wafer, e.g. for the pyramidal hole defects, they more likely originate from the substrate. In the case of the oval holes (InGaAs, Fig. 2) and the boat defects (InP, Fig. 3), the size of the defects differ over a wafer. Therefore, their origin should not exclusively be due to the substrate surface but additionally the growth conditions [20,21] describe tear drop like defects growing on exactly oriented (0 0 1) InP substrates. In our investigations we have not observed them, probably due to the utilised high growth temperatures with $T_g \geq 660^\circ\text{C}$ and the high defect densities at lower growth temperatures. Neither were in-rich hillocks observed at low growth temperatures [14].

References

- [1] T. Terakado, K. Tsuruoka, I. Ishida, T. Nakamura, K. Fukushima, S. Ae, A. Uda, T. Torikai, T. Uji, *Electron. Lett.* 31 (1995) 2182.
- [2] M. Gerhardt, G. Kirpal, G. Benndorf, R. Schwabe, R. Franzheld, V. Gottschalch, J. Kovac, M. Druminski, EW MOVPE VII, Berlin, June 1997, paper H12.
- [3] A.S. Jordan, A. Robertson, J.L. Zilko, *Appl. Phys. Lett.* 64 (1993) 360.
- [4] H. Hardtdegen, M. Hollenfelder, R. Meyer, R. Carius, H. Mühndler, S. Frohnhoff, D. Szyuka, H. Lüth, *J. Crystal Growth* 124 (1992) 420.
- [5] H. Hardtdegen, P. Giannoulas, V–III Review 11 (5) (1998) 34.
- [6] H. Roehle, H. Schroeter-Jansen, R. Kaiser, *J. Crystal Growth* 170 (1997) 109.
- [7] C.C. Hsu, Y.F. Yang, H.J. Ou, E.S. Yang, H.B. Lo, *Appl. Phys. Lett.* 71 (1997) 3248.
- [8] G. Zimmermann, A. Ougazzaden, A. Gloukhian, E.V.K. Rao, D. Delprat, A. Ramdane, A. Mircea, *Mater. Sci. Eng. B* 44 (1997) 37.
- [9] Table on CVD Metalorganics Vapor Pressure Data, Morton International Inc., Danvers, USA, 1997.
- [10] H. Heinecke, E. Veuhoff, N. Pütz, M. Heyen, P. Balk, *J. Electron. Mater.* 13 (1984) 815.
- [11] G. Landgren, Z. Paska, J. Wallin, K. Streubel, EW MOVPE V, Malmö, 1993.
- [12] H.C. Chui, R.M. Biefeld, B.E. Hammons, W.G. Breiland, T.M. Brennan, E.D. Jones, H.K. Moffat, *J. Electron. Mater.* 26 (1997) 37.
- [13] K. Streubel, J. Wallin, G. Landgren, U. Öhlander, S. Lourdudoss, O. Kjebon, *J. Crystal Growth* 143 (1994) 7.
- [14] H. Protzmann, F. Höhnsdorf, Z. Spika, W. Stolz, E.O. Göbel, M. Müller, J. Lorberth, *J. Crystal Growth* 170 (1997) 155.
- [15] Y.F. Yang, C.C. Hsu, E.S. Yang, *Electron. Lett.* 30 (22) (1994) 1894.
- [16] M. Ogasawara, K. Sato, Y. Kondo, *Appl. Phys. Lett.* 60 (1992) 1217.
- [17] U. Bangert, A.J. Harvey, C. Dieker, H. Hardtdegen, *Appl. Phys. Lett.* 69 (14) (1996) 2101.
- [18] S.P. Watkins, H.D. Cheung, G. Knight, G. Kelly, *Appl. Phys. Lett.* 68 (1996) 1960.
- [19] D. Keiper, R. Westphalen, G. Landgren, presented at the 40th EMC 1998, Virginia.
- [20] D. Franke, N. Grote, EW MOVPE VII, Berlin, June 1997, paper G4.
- [21] M. Nakamura, S. Katsura, N. Makino, E. Ikeda, K. Suga, R. Hirano, *J. Crystal Growth* 129 (1993) 456.