

JOURNAL DE PHYSIQUE

LEHIGH UNIVERSITY LIBRARIES



3 9151 00586805 0



Volume 5
Colloque n° 5
Suppl. JP II, n° 6

IV

Proceedings of the Tenth European Conference
on Chemical Vapour Deposition

Volume II

ISSN 0021-8995/83/0005-0000\$02.50/0



Recognized by the European Physical Society

Published under the supervision and responsibility of the French Physical Society



Physique

530.5
J86C2
V.5
1995
Coll. 5
Pt. 2

DATE DUE



Proceedings of the Tenth European Conference on Chemical Vapour Deposition



Jesolo Lido, Venice, Italy
September 10-15, 1995

Volume II

Edited by: Giovanni A. Battiston
Rosalba Gerbasi
Marina Porchia

les éditions

de physique

Avenue du Hoggar
Zone Industrielle de Courtaboeuf
B.P. 112
91944 Les Ulis cedex A, France

Commission paritaire N° 57920

© Les Editions de Physique 1995

Directrice de la Publication : Jeanne BERGER

Imprimé en France. — JOUVE, 18, rue Saint-Denis, 75001 PARIS
N° 228616B. Dépôt légal : Août 1995

CONTENTS

Volume I

Fundamentals

Morphology and Film Growth in CVD Reactions V. Hlavacek, J.J. Thiart and D. Orlicki	C5-3
Modeling of Mass Transport and Gas Kinetics of the Reactive Sputtering Process S. Berg and C. Nender	C5-45
Strained Si _{1-x} Ge _x /Si Dots and Wires Grown by Selective Epitaxy L. Vescan, R. Loo, A. Souifi, C. Dieker and S. Wickenhäuser	C5-55
Thermochemical and Mass Transport Modelling of the Chemical Vapour Deposition of Si _{1-x} Ge _x M. Pons, E. Blanquet, C. Bernard, H. Rouch, J.M. Dedulle and R. Madar	C5-63
Kinetic Modeling of the Gas Phase Decomposition of Germane by Computational Chemistry Techniques M. Hierlemann, H. Simka, K.F. Jensen and M. Utz.....	C5-71
Thermodynamic Analysis of the Chemical Vapor Deposition of Phosphorus Nitride (P ₃ N ₅) Thin Films S. Eroglu	C5-79
Metal-Containing Thin Film MOCVD: Kinetics and Reaction Mechanisms I. Fragalà.....	C5-87
Mass Spectrometric Study of the Gas Phase During Chemical Vapor Deposition of Pyrolytic Carbon F. Fau-Canillac, F. Carrere, A. Reynes, C. Vahlas and F. Maury	C5-89
Monitoring of SiC Deposition in an Industrial CVI/CVD Reactor by In-Situ FTIR Spectroscopy H. Mosebach, V. Hopfe, M. Erhard and M. Meyer	C5-97
Kinetic Processes in the CVD of SiC from CH ₃ SiCl ₃ -H ₂ in a Vertical Hot-Wall Reactor F. Langlais, F. Loumagne, D. Lespiaux, S. Schamm and R. Naslain.....	C5-105
On the Deposition Kinetics of the LPCVD Gate Oxides Prepared from SiH ₄ and O ₂ J.B. Rem, J.H. Klootwijk, C. Cobianu, J. Holleman and J.F. Verweij.....	C5-113
Deposition of Platinum from Bis(Acetylacetonato)Platinum(II) J. Arndt, L. Klippe, R. Stolle and G. Wahl.....	C5-119

Experimental Design Approach to Development of a CVD ZrN Coating W.C. Russell.....	C5-127
Silicon Carbide Coating for Carbon Materials Produced by a Pack-Cementation Process O. Paccaud and A. Derré	C5-135
Chemical Vapour Deposition of Thick Tungsten Coatings: Raman Measurements and Mass Transport Modelling M. Pons, A. Benezech, P. Huguet, R. Gaufres, Ph. Diez and D. Lafforet.....	C5-143
Thermodynamic Simulation of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ Film Growth Using Aerosol MOCVD F. Weiss, A. Pisch, C. Bernard and U. Schmatz.....	C5-151
Modelling Binary, Knudsen and Transition Regime Diffusion Inside Complex Porous Media G.L. Vignoles	C5-159
Kinetics of Chemical Vapour Deposition of Boron Nitride from a Gas Mixture of Trimethylborazine, Ammonia, and Hydrogen at 900 to 1050 °C and 1 Bar Total Pressure A. Jörg, D. Neuschütz and E. Zimmermann.....	C5-167
Parameters of Vacuum Process as the Factors Changing the Growth Kinetics of Chromized Layers Produced on Low-Carbon Iron Alloys by Means of CVD E. Kasprzycka.....	C5-175
A Study of CVD of Gallium Nitride Films by In Situ Gas-Phase UV Spectroscopy S.E. Alexandrov, A.Y. Kovalgin and D.M. Krasovitskiy	C5-183
Mass Spectrometric Study of Thermolysis Mechanism of Metal Acetylacetonates Vapour A.F. Bykov, A.E. Turgambaeva, I.K. Igumenov and P.P. Semyannikov.....	C5-191
Thermodynamics Aspects of Chemical Vapour Deposition of V-VII Group Metals and their Alloys with Tungsten Y.V. Lakhotkin.....	C5-199
Mechanism of Thermal Decomposition of Palladium β -Diketonates Vapour on Hot Surface P.P. Semyannikov, V.M. Grankin, I.K. Igumenov and A.F. Bykov.....	C5-205
Mechanism of Interaction of Dimethylgold(III) Chelates Vapour with Hot Surface P.P. Semyannikov, V.M. Grankin, I.K. Igumenov and G.I. Zharkova.....	C5-213
Mass Spectrometric Study of Copper(II) β -Diketonates Vapour Thermolysis Mechanism and Kinetics A.E. Turgambaeva, A.F. Bykov and I.K. Igumenov	C5-221
Deposition Kinetics of CVD-Silicon Carbonitride Coatings A.G. Varlamov and S.V. Afanas'eva	C5-229

CVD as Laminar Phenomena with Homogeneous/Heterogeneous Appearances.

A Theoretical Analysis

K.T. Raic C5-235

Growth Modelling

In-Situ Diagnostics of CVD Processes, the Key to Growth Modelling

M. Pemble⁽¹⁾

Modelling of Precursor Flow and Deposition in Atomic Layer Deposition Reactor

H. Siimon and J. Aarik C5-245

Simulation of Chemical Vapour Deposition of SiC from Methyltrichlorosilane in a Hot Wall Reactor

D. Neuschütz, M. Schierling and S. Zimdahl C5-253

Simulation of Epitaxial Silicon Chemical Vapor Deposition in Barrel Reactors

M. Masi, S. Fogliani and S. Carrà C5-261

Optimum Design of LPCVD Reactors

L.M. Zambov C5-269

Reactivities of TaCl₅ and H₂O as Precursors for Atomic Layer Deposition

H. Siimon and J. Aarik C5-277

Systematic Classification of LPCVD Processes

J. Schlote, K. Tittelbach-Helmrich, B. Tillack, B. Kuck and T. Hünlich C5-283

Low Pressure CVD of Silicon Nitride from a Silane-Ammonia Mixture: Analysis of Preliminary Experimental and Simulation Results

K. Yacoubi, C. Azzaro and J.P. Couderc C5-291

Wall-Less Like Reactor: Simulation and Experimental Results

C. Bisch, Y.B. Wang and F. Teyssandier C5-299

Reactor Modelling and Analysis of Amorphous Hydrogenated Silicon Deposition by PECVD

A. Djelloul, B. Despax, J.P. Couderc and P. Duverneuil C5-307

SIPOS Deposition from Disilane: Experimental Study and Modelling

C. Cordier, E. Dehan, E. Scheid, P. Duverneuil and J.P. Couderc C5-315

Economical Analysis and Optimization of a Low Pressure Chemical Vapor Deposition (LPCVD) Reactor

T. Tamani, P. Duverneuil and J.P. Couderc C5-323

Modelling of the Deposition of Molybdenum on Silicon from Molybdenum Hexafluoride and Hydrogen

E.N. Orij, M.H.J.M. de Croon and G.B. Marin C5-331

⁽¹⁾Article not received by the publisher

Formation of Ti(OCN) Layers Under Glow Discharge Conditions J.R. Sobiecki and T. Wierzchon	C5-339
---	--------

High T_c Superconductors

Anisotropic Materials Prepared by CVD: Organic Molecular Conductors and High T_c Superconductors A. Figueras.....	C5-347
A Study by In Situ FTIR Spectroscopy of the Decomposition of Precursors for the MOCVD of High Temperature Superconductors A.Y. Kovalgin, F. Chabert-Rocabois, M.L. Hitchman, S.H. Shamlan and S.E. Alexandrov.....	C5-357
High Quality $YBa_2Cu_3O_{7-x}$ Superconducting Thin Films Grown by MOCVD C. Dubourdieu, J.P. Sénateur, O. Thomas and F. Weiss	C5-365
Barium Diketonates as Precursors for HTSC Thin Films: Structure and Properties A. Drozdov and S. Troyanov.....	C5-373
Atomic Layer-by-Layer MOCVD of Oxide Superconductors S. Oda, S. Yamamoto and A. Kawaguchi	C5-379
MOCVD Routes to $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ Superconductor and Dielectric Insulator Thin Films B.J. Hinds, D.B. Studebaker, J. Chen, R.J. McNeely, B. Han, J.L. Schindler, T.P. Hogan, C.R. Kannewurf and T.J. Marks	C5-391
MOCVD of High Quality $YBa_2Cu_3O_{7-\delta}$ Thin Films Using Novel Fluorinated and Non-Fluorinated Precursors B.C. Richards, S.L. Cook, D.L. Pinch and G.W. Andrews.....	C5-407
Compositional Effects on Morphology, Structure and Superconducting Properties of $Y_xBa_yCu_zO_{7-\delta}$ Thin Films Prepared by Metalorganic Chemical Vapour Deposition M. Doudkowsky, J. Santiso, A. Figueras and R. Berjoan	C5-415
Growth of $(YBaCuO)_m/(PrBaCuO)_n$ Superlattices by MOCVD N. Didier, B. Chenevier, O. Thomas, J.P. Sénateur, F. Weiss and A. Gaskov.....	C5-423
Physico-Chemical Study of Barium (II) Dipivaloylmethanate Nature N.E. Fedotova, I.K. Igumenov, V.I. Mamatyuk and G.V. Sidorenko	C5-431
Preparation of YBCO on YSZ Layers Deposited on Silicon and Sapphire by MOCVD: Influence of the Intermediate Layer on the Quality of the Superconducting Film G. Garcia, J. Casado, J. Llibre, M. Doudkowsky, J. Santiso, A. Figueras, S. Schamm, D. Dorignac, Ch. Grigis and M. Aguilò	C5-439

MOCVD

Recent Trends in the Selection of Metal-Organic Precursors for MOCVD Process F. Maury	C5-449
Nickel Thin Films Grown by MOCVD Using Ni(dmg) ₂ as Precursor M. Becht, J. Gallus, M. Hunziker, F. Atamny and K.-H. Dahmen	C5-465
Vanadium Oxi-Carbide Coatings Deposited by OMCVD in an Isothermal Reactor L. Poirier and F. Teyssandier.....	C5-473
Growth of InP in a Novel Remote-Plasma MOCVD Apparatus: an Approach to Improve Process and Material Properties G. Bruno, P. Capezzuto and M. Losurdo.....	C5-481
MOCVD of Noble Metals I.K. Igumenov.....	C5-489
Design of Zr(IV) and Hf(IV) Co-Ordination Compounds - Precursors for MOCVD Synthesis of Protective Coatings A. Grafov, E. Mazurenko, G.A. Battiston and P. Zanella	C5-497
New Barium Volatile Complexes Useful in CVD A. Drozdov, S. Troyanov, A. Pisarevsky and Y. Struchkov	C5-503
Deposition of MoO ₃ Films from a Volatile Molybdenyl Complex B. Ballarin, E. Brescacin, G.A. Rizzi and E. Tondello.....	C5-509
CVD Copper Deposition from Cu ^I (HFAC)TMVS Studied Through a Modeling Experimental Design J.-L. Mermet, M.-J. Mouche, F. Pires, E. Richard, J. Torres, J. Palteau and F. Braud	C5-517
Chemical Vapor Deposition of ZrO ₂ Thin Films Using Zr(NEt ₂) ₄ as Precursor A. Bastianini, G.A. Battiston, R. Gerbasi, M. Porchia and S. Daolio	C5-525
Properties of Thin Epitaxial Aerosol MOCVD CeO ₂ Films Grown on (1102) Sapphire K. Fröhlich, J. Souc, D. Machajdik, A.P. Kobzev, F. Weiss, J.P. Senateur and K.H. Dahmen.....	C5-533
Structure and Destruction of a Precursor: Mass-Spectrometric Evaluation of Creation of Functional Films with Predetermined Composition A. Grafov, I.A. Grafova, E. Mazurenko, L.I. Koval, S. Catinella, P. Traldi, G.A. Battiston and P. Zanella.....	C5-541
Volatile Metals Coordination Compounds as Precursors for Functional Materials Synthesis by CVD-Method E.A. Mazurenko and A.I. Gerasimchuk	C5-547
CVD Synthesis of HTSC Films Using Volatile Coordination Compounds S.V. Volkov, V.Y. Zub, O.N. Balakshina and E.A. Mazurenko	C5-553

XIV

A New Route to the Deposition of Al_2O_3 by MOCVD A.C. Jones, D.J. Houlton, S.A. Rushworth and G.W. Critchlow	C5-557
--	--------

CVD History

CVD Conference Recollections J.M. Blocher Jr.	C5-563
---	--------

Volume II

Activated Methods

Remote PECVD: a Route to Controllable Plasma Deposition S.E. Alexandrov	C5-567
Plasma-Assisted Deposition at Atmospheric Pressure J. Salge	C5-583
Remote Microwave Plasma Enhanced Chemical Vapour Deposition of Amorphous Carbon: Optical Emission Spectroscopy Characterisation of the Afterglow and Growth Rates C. Tixier, P. Tristant, J. Desmaison and D. Merle	C5-593
Laser-CVD 3D Rapid Prototyping of Laser Driven Moveable Micro-Objects O. Lehmann and M. Stuke	C5-601
Optical Emission Analysis of a $\text{Si}(\text{CH}_3)_4$ -Argon Radio Frequency Plasma for SiC Films Deposition M. Andrieux, J.M. Badie, C. Bisch, M. Ducarroir and F. Teyssandier	C5-607
Deposition and Properties of Thin PECVD Carbon Films After Rapid Thermal Annealing G. Beshkov, D. Dimitrov, S. Georgiev and T. Dimitrova	C5-615
Remote Microwave Plasma Enhanced Chemical Vapour Deposition of SiO_2 Films: Oxygen Plasma Diagnostic C. Regnier, J. Desmaison, P. Tristant and D. Merle	C5-621
Growth Kinetics of Copper Films from Photoassisted CVD of Copperacetylacetonate D. Tonneau, R. Pierrisnard, H. Dallaporta and W. Marine	C5-629
Deposition of Boron Containing Coatings Using MO-PACVD Process to Protect Aluminium Casting Tools K.-T. Rie, A. Gebauer and C. Pfohl	C5-637

Laser CVD vs. Hot Wall CVD: Coating of Fibres for Ceramic Composites V. Hopfe, K. Brennfleck, R. Weiß, R. Meistring, K. Schönfeld, R. Jäckel, G. Dietrich and R. Goller	C5-647
Principles for Controlling the Electronic Quality of High-Rate Deposited a-Si:H Films G. Suchaneck, T. Blum, S. Röhlecke and A. Kottwitz.....	C5-655
On the Use of H ₂ Plasma for the Cleaning and Passivation of InP Substrates G. Bruno, M. Losurdo and P. Capezzuto.....	C5-663
Preparation of Bismuth Titanate Films by Electron Cyclotron Resonance Plasma Sputtering- Chemical Vapor Deposition H. Masumoto and T. Hirai.....	C5-671
A Comparative Study of Iron-Based Film Deposition from Iron Pentacarbonyl at 248 nm and 488 nm I. Voicu, R. Alexandrescu, R. Cireasa, I. Morjan, D.C. Dumitras, S. Mulenکو, A. Pogorelyi and A. Andrei	C5-679
Direct Deposition of Metal Film Patterns Using Nitrogen Laser E.F. Reznikova, V.V. Chesnokov, G.I. Zharkova and I.K. Igumenov	C5-687
The Study of the Boron Nitride Thin Layer Structure G.S. Yuryev, E.A. Maximovskiy, Yu.M. Rumyantsev, N.I. Fainer and M.L. Kosinova.....	C5-695
Properties of Surface Layers Produced from a Metalorganic Titanium Compound Under Glow Discharge Conditions T. Wierzchon and J.R. Sobiecki	C5-699
PE MOCVD of Thin High Transparent Dielectric Amorphous Films of Aluminium Oxide V.P. Ovsyannikov, G.V. Lashkaryov and E.A. Mazurenko	C5-705
Low Temperature Plasma Enhanced CVD Synthesis of Piezoactive ZnO Films T.V. Tabenskaya, V.P. Ovsyannikov and E.A. Mazurenko	C5-711

Ceramics and Coatings

Low Temperature Deposition of TiN Ceramic Material by Metal Organic and/or Plasma Enhanced CVD C.I.M.A. Spee, J.P.A.M. Driessen and A.D. Kuypers.....	C5-719
Silicon and Boron Containing Components by CVD and CVI for High Temperature Ceramic Composites L. Vandenbulke and M. Leparoux.....	C5-735
Murakami and H ₂ SO ₄ /H ₂ O ₂ Pretreatment of WC-Co Hard Metal Substrates to Increase the Adhesion of CVD Diamond Coatings R. Haubner, S. Kubelka, B. Lux, M. Griesser and M. Grasserbauer.....	C5-753

Deposition of Boron Nitride Films from BB'B"-Trichloroborazine R. Stolle and G. Wahl.....	C5-761
LPCVD Pyrocarbon Coating on Unidirectional Carbon Fiber Yarns: an Efficient Interphase for Aluminium Matrix Composites P. Bertrand, M.H. Vidal-Setif and R. Mevrel.....	C5-769
Preparation of β -SiC Coatings Using 1,2-Dimethyldisilane as Precursor X. Tang, R. Haubner, B. Lux, A. Zechmann and E. Hengge	C5-777
Chemical Vapour Deposition of AlN-Si ₃ N ₄ Codeposits F. Henry, B. Armas, C. Combescure, D. Thenegal and R. Flamand.....	C5-785
SiCN Amorphous Materials Chemical Vapour Deposited Using the Si(CH ₃) ₄ -NH ₃ -H ₂ System A. Bendeddouche, R. Berjoan, E. Bêche, S. Schamm, V. Serin, R. Carles and R. Hillel.....	C5-793
TiN-Ti _x Si _y Codeposits A.P.C.V.D. Produced Using the TiCl ₄ -N ₂ -SiH ₂ Cl ₂ - H ₂ System G. Llauro, A. Bendeddouche, M. Nadal and R. Hillel	C5-801
Optimization of the Deposition Conditions of Titanium Nitride from Ammonia and Titanium Tetrachloride M. Nadal and F. Teyssandier.....	C5-809
Refractory Coatings of C-Me-Si and C-Me-B-Si Systems for Protection of Carbon Materials (CM) S.G. Andryushin and A.V. Kasatkin	C5-815
Heat-Resistance and Phase Composition of Ti-Si Coatings on Niobium A.V. Kasatkin, S.U. Rybakov and G.M. Anurova.....	C5-823
Development of TiN-Si ₃ N ₄ Nano Composite Coatings for Wear Resistance Applications A.G. Dias, J.H. van Breda, P. Moretto and J. Ordelman	C5-831
Characterization	
Optical Properties of CVD-Deposited Dielectric Films for Microelectronic Devices A. Sassella, A. Borghesi, S. Rojas and L. Zanotti.....	C5-843
Photoelectron Diffraction: a Structural Probe for Epitaxial Thin Films G. Granozzi.....	C5-861
Characterization of Buffer Layers for SiC CVD V. Cimalla, J. Pezoldt, G. Ecke, H. Rößler and G. Eichhorn	C5-863
Substrate Effects on the APCVD Growth of Titanium Nitride Films S.E. Johnson and J.R. Owen.....	C5-871

Analysis of the Intermediate Layers Generated at the Film-Substrate Interface During the CVD Process of Diamond Synthesis M.L. Terranova, V. Sessa, M. Rossi, G. Vitali, G. Cappuccio and C. Veroli.....	C5-879
Influence of the Doping Gas on the Axial Uniformity of the Growth Rate and the Electrical Properties of LPCVD In-Situ Doped Polysilicon Layers D. Briand, M. Sarret, P. Duverneuil, T. Mohammed-Brahim and K. Kis-Sion.....	C5-887
Investigation of the Substrate/Epitaxial Interface of Si/Si _{1-x} Ge _x Layers Grown by LPCVD R. Loo, L. Vescan, C. Dieker, D. Freundt, A. Hartmann and A. Mück.....	C5-895
Transmission Electron Microscopy Studies of (AlN-Si ₃ N ₄) Codeposits Obtained by LPCVD P. Marti, F. Henry, A. Mazel, B. Armas and J. Sevely.....	C5-905
Polycrystalline Silicon Characteristics Dependence on Starting Amorphous Material T. Mohammed-Brahim, M. Sarret, D. Briand, K. Kis-Sion, O. Bonnaud and A. Hadjaj.....	C5-913
Oxygen Effect on the Stability of PECVD Boron-Carbon Films S.Yu. Rybakov, V.M. Sharapov and L.E. Gavrilov.....	C5-921
HREM Characterization of Interfaces in Thin MOCVD Superconducting Films D. Dornigac, S. Schamm, Ch. Grigis, J. Santiso, G. Garcia and A. Figueras.....	C5-927
New Methods and Materials	
Atomic Layer Epitaxy in Deposition of Various Oxide and Nitride Thin Films M. Leskelä and M. Ritala.....	C5-937
Laser-Induced Chemical Vapour Deposition of Silicon Carbonitride W.F.A. Besling, P.J.J.M. van der Put and J. Schoonman.....	C5-953
Mass Flow Controlled Evaporation System H.J. Boer.....	C5-961
Low Pressure CVD of Tungsten Carbides P. Tägtström, H. Högberg, U. Jansson and J.-O. Carlsson.....	C5-967
Chemical Vapour Deposition for Optical Fibre Technology L. Cognolato.....	C5-975
Diamond Deposition Using a Grid Filament D.M. Li, T. Mäntylä and J. Levoska.....	C5-989
Deposition of Thick Layers, in a New CVD Reactor H. Vergnes, E. Scheid, P. Duverneuil and J.P. Couderc.....	C5-997

Thin Film Carbon Coating for Application in Implantable Prostheses

F. Vallana, P. Arru and C. Stacchino⁽²⁾LPCVD SiO₂ Layers Prepared from SiH₄ and O₂ at 450 °C in a Rapid Thermal Processing Reactor

C. Cobianu, J.B. Rem, J.H. Klootwijk, M.H.H. Weusthof, J. Holleman and

P.H. Woerlee C5-1005

Preparation of Ultrafine CVD WC Powders Deposited from WCl₆ Gas Mixtures

X. Tang, R. Haubner, B. Lux and B. Kieffer C5-1013

Atomic Layer Epitaxy Growth of AlN Thin Films

K.-E. Elers, M. Ritala, M. Leskelä and L.-S. Johansson C5-1021

Thin Films of Zirconia-Phosphate Glasses Deposited by an Aerosol CVD Process

J.L. Deschanvres, J.M. Vaca and J.C. Joubert C5-1029

OMCVD on Fluidized Divided Substrates: a Potential Method for the Preparation of Catalysts

R. Feurer, A. Reynes, P. Serp, P. Kalck and R. Moranco C5-1037

Evolution of Magnetomechanical and Magnetic Properties of Siliconized Iron-Silicon Alloys by CVD Process Using SiCl₄

S. Crottier-Combe, S. Audisio, J. Degauque, C. Beraud, F. Fiorillo, M. Baricco and

J.L. Porteseil C5-1045

Growth Stability in Semiopen Physical Vapour Transport

C. Paorici, M. Zha, L. Zanotti, L. Carotenuto and T. Tiberti C5-1053

Vapour Growth of Micro-Coiled Ceramic Fibers and their Properties

S. Motojima, I. Hasegawa and H. Iwanaga C5-1061

Preparation of Onboard Reforming Catalyst for Methanol by Chemical Vapor Deposition

M. Yano, K. Ohno and H. Imanaka C5-1069

Processes for New Industrial Applications

Processes for New Industrial Applications

G. Lengeling⁽³⁾

Deposition of Oxide Layers by Computer Controlled "Injection-LPCVD"

F. Felten, J.P. Senateur, F. Weiss, R. Madar and A. Abrutis C5-1079

Deposition and Study of Niobium Coating on Iron and Copper Substrates from Reduction of NbCl₅ by Hydrogen or Vapors of Zinc

S. Audisio, H. Hamed and D. Hertz C5-1087

⁽²⁾ Article not received by the publisher⁽³⁾ Article not received by the publisher

Electronic and Optoelectronic Materials

Chemical Vapor Deposition of Hyperpure Polysilicon on Industrial Scale M. Domenici.....	C5-1099
Atomic Layer-by-Layer Epitaxy of Silicon and Germanium Using Flash Heating in CVD J. Murota, M. Sakuraba, T. Watanabe, T. Matsuura and Y. Sawada	C5-1101
Plasma-Enhanced Chemical Vapour Deposition of Amorphous Se Films P. Nagels, E. Slegers and R. Callaerts	C5-1109
Delta Doping in Si and SiGe by LP(RT)CVD B. Tillack, J. Schlote, G. Ritter, D. Krüger, G. Morgenstern and P. Gaworzewski	C5-1117
Powder Dissipation in PECVD for $\text{SiH}_4\text{-CH}_4\text{-H}_2$ Gas Mixtures P. Rava, G. Crovini, F. Demichelis, F. Giorgis, R. Galloni, R. Rizzoli and C. Summonte	C5-1125
Comparison Between CVD and ALE Produced TiO_2 Cathodes in $\text{Zn}/(\text{PEO})_4\text{ZnCl}_2/\text{TiO}_2$, SnO_2 or ITO Galvanic Cells A. Turkovic, A. Drasner, D. Sokcevic, M. Ritala, T. Asikainen and M. Leskelä	C5-1133
Morphology and Thermal Stability of Me-Si-N (Me=Re, W, Ta) for Microelectronics A.-M. Dutron, E. Blanquet, V. Ghetta, R. Madar and C. Bernard	C5-1141
Amorphous Hydrogenated Silicon Nitride Deposited by Mercury Photosensitization Chemical Vapour Deposition for Optoelectronic Applications P. Pastorino, G. Morello and S. Tamagno	C5-1149
Production and Characterization of Quantum Nanostructures of Epitaxial Semiconductors M. Berti, A.V. Drigo, M. Mazzer, A. Camporese, G. Torzo and G. Rossetto	C5-1157
Low-Temperature Epitaxial Growth Mechanism of $\text{Si}_{1-x}\text{Ge}_x$ Films in the Silane and Germane Reactions J. Murota, Y. Takasawa, H. Fujimoto, K. Goto, T. Matsuura and Y. Sawada	C5-1165
Physical Properties of Gallium Indium Nitride Films Prepared by Photo-Assisted MOVPE T. Nagatomo and O. Omoto	C5-1173
Author Index.....	C5-1179

Atomic Layer Epitaxy in Deposition of Various Oxide and Nitride Thin Films

M. Leskelä and M. Ritala

Department of Chemistry, University of Helsinki, P.O. Box 6, FIN-00014 Helsinki, Finland

Abstract. Atomic Layer Epitaxy (ALE) is a chemical vapor phase thin film deposition method which is based on saturative surface reactions. As the film is growing in a self-limiting manner ALE is a promising method to deposit thin, high-quality films for micro- and optoelectronics. In the present paper the deposition of different dielectric oxides, conducting oxides as well as nitrides is reviewed giving emphasis to precursors and their effect on growth mechanisms and film properties.

1. INTRODUCTION

The development in microelectronics is connected to the development of thin film technologies. For example in silicon technology the ULSI chips need nanoscale components. This size reduction requires improving process control, lower processing temperatures to prevent diffusion, better definition and quality of interfacial regions [1,2]. This means that there is a permanent need for better thin film deposition processes and new materials.

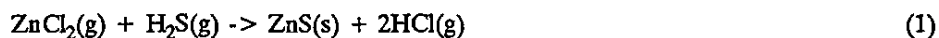
In recent years there has been considerable activity on the deposition of metal oxide thin films on a variety of substrate materials. Oxides are known from their chemical inertness, good high temperature properties and resistance to oxidation. Characteristic for oxide thin films is their optical transparency, high electrical resistivity, low thermal conductivity, diamagnetism and chemical stability [3]. Exceptions exist, of course, and some oxides are conducting and even superconducting. Oxide thin films are interesting because of their many applications in microelectronic [4,5], optoelectronic [6-8] and superconducting [9,10] devices. The function of the oxide films in these devices may be insulating, conducting, superconducting or they may be used as buffer or protecting layers.

Nitride films can be divided in two groups: transition metal nitrides and nitrides of the main group elements from which the most important are Si_3N_4 , BN, AlN and GaN. The nitride films of the main group elements are used as passivation and dielectric layers [11] and GaN as a wide band gap (3.4 eV) semiconductor in optoelectronic devices [11,12]. The transition metal nitride films, especially TiN, are extensively used as wear resistant coatings on cutting tools and as diffusion barriers and nucleation layers in semiconductor devices [13,14]. Owing to the need of an improved conformality, the deposition of nitride films by chemical methods instead of a physical ones has gained growing attention.

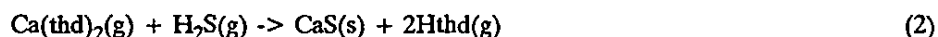
Atomic Layer Epitaxy (ALE) with its self-limiting growth process is a promising method to fulfil the requirements in controlled deposition of high-quality thin films and stacks of thin films with tailored interfaces. In the present paper the investigations on ALE deposition of different oxide (Ti, Zr, Hf, Al, Ta, In, Zn, Sn) and nitride (Nb, Ti, Al, Ga, In) thin films are reviewed.

2. ALE METHOD

In ALE the reactant vapors are pulsed onto the substrate alternately one at a time and purged with an inert gas between the reactant pulses. With a proper adjustment of the experimental conditions it is possible to get an exact one monolayer of the reactant to chemisorb on the surface. The real growth rate is often lower than one monolayer/cycle because of the steric hindrances of the chemisorbed precursor molecules [15]. For example in the growth of ZnS by the reaction (Fig. 1)



2-3 cycles are needed for a complete monolayer [16], but the reaction



(thd = 2,2,6,6-tetramethyl-3,5-heptanedione) needs 5-6 cycles for the formation of a CaS monolayer [17]. The special feature of the ALE method is, however, that the growth rate is self-controlled and stable in a certain temperature range, "ALE-window" [18]. Thus the thickness of the film can be controlled by the number of reaction cycles.

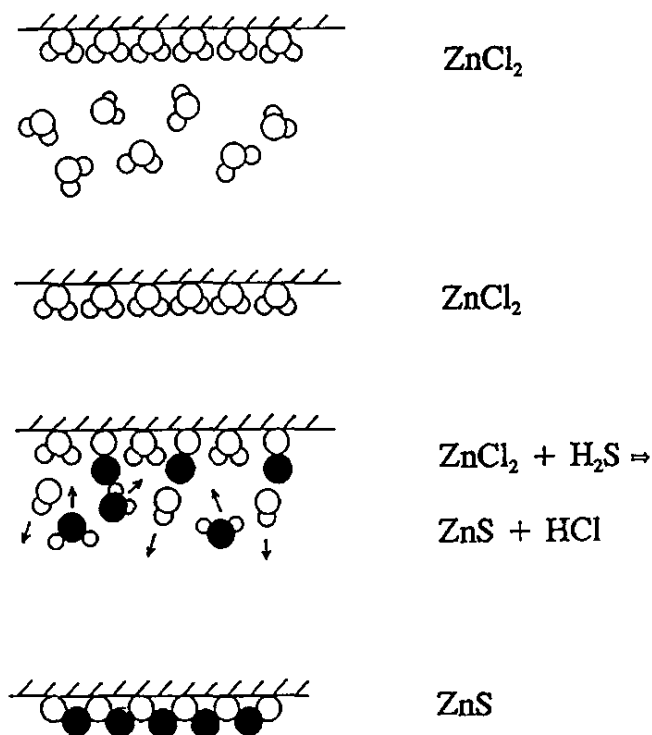


Figure 1. The principle of the ALE-process showing the growth of ZnS film from ZnCl_2 and H_2S .

2.1 Characteristic features of ALE

The characteristic features of ALE and their implications to the process are summarized in Table 1. The obvious advantages are listed as well.

Disadvantages of the ALE method are slow growth rate and low precursor utilization efficiency. These disadvantages can be compensated by reactor and precursor design. The semiclosed travelling wave reactors allow the use of large substrate batches [19]. The precursors preferred in ALE, contradictory to CVD, are those reacting aggressively with each other.

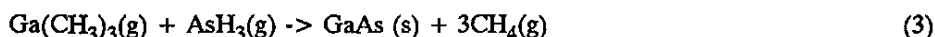
The crystallinity in the thin films depends on the substrate and film material. In ALE single crystalline, "epitaxial" films are obtained if single crystal substrates are employed. In large area applications, like electroluminescent (EL) devices, however, cheap amorphous glass substrates have to be used. The ALE films deposited on glass are amorphous or polycrystalline depending on the film composition. Since the word epitaxy is generally used only in connection to the growth of single crystal films, the use of term ALE in deposition of amorphous films has led to some misunderstandings. Therefore very different names have been adapted to the processes carried out according to the principles of ALE: atomic layer deposition, chemical vapor atomic layer deposition, atomic layer growth, successive layer-wise chemisorption, pulsed beam chemical vapor deposition, sequential surface chemical reaction growth, molecular layer epitaxy and digital layer epitaxy [18,20]. Especially atomic layer deposition is gaining more acceptance [21-24]. In this paper the term ALE is used in its original meaning: growth of thin films in a self-controlled manner using alternate dosing of the reactants. In this meaning ALE covers the deposition of amorphous, polycrystalline and single crystalline thin films.

Table 1. Summary of the characteristic features of ALE, their implications on the film growth and the consequent practical advantages.

Characteristic feature of ALE	Inherent implication on film deposition	Practical advantage
Self-limiting growth process	Film thickness is dependent only on the number of deposition cycles	Accurate and simple thickness control
	No need of reactant flux homogeneity	Large area capability Large batch capability Excellent conformality No problems with inconstant vaporization rates of solid precursors Good reproducibility Straightforward scale-up
	Atomic level control of material composition	Capability to produce sharp interfaces and superlattices Possibility to interface modification
Separate dosing of reactants	No gas phase reactions	Favors precursors highly reactive towards each other, thus enabling effective material utilization
	Sufficient time is provided to complete each reaction step	High quality materials are obtained at low processing temperatures
Processing temperature windows are often wide	Processing conditions of different materials are readily matched	Capability to prepare multilayer structures in a continuous process

2.2 Equipments

ALE growth has been realized in different reactor types. In the growth of epitaxial III-V or II-VI semiconductors on single crystalline substrates low-pressure MBE reactors have been employed [25,26]. Several modifications, including MOVPE type sources for metalorganics and hydrides in a MBE reactor [27], small MOVPE type reactor [28] or moving and rotating substrates for the pulsing of the reactants [29-31], have been developed. The use of laser irradiation may enhance the surface reactions and film growth. For example in the reaction



one monolayer per cycle growth has been obtained when laser irradiation was used during the exposure of $\text{Ga}(\text{CH}_3)_3$ [32,33]. In the deposition of polycrystalline and amorphous films the flow type reactor is most often used [34,35]. The precursors having vapor pressure high enough at room temperature may be dosed into the reactor from external reservoirs by means of their own pressure while low vapor pressure reactants are vaporized from open boats inside the reactor. The pulsing of the latter is accomplished by inert gas valving [36]. The substrates may locate in the reactor face to face separated by a narrow channel or back to back leaving a more open reactor space. The experiments and results mainly reviewed in this paper have been carried out in a narrow channel reactor made by Microchemistry Ltd, Espoo, Finland [35]. In the narrow channel the precursor molecules undergo numerous collisions with the substrate surfaces which makes the adsorption more probable, fastens the growth and improves the precursor utilization. This all means that short pulse and purge times (< 0.5 s) are possible.

2.3 ALE activities

The ALE method was developed by Suntola *et al.* [37] about twenty years ago when they studied new deposition methods to fabricate thin film electroluminescent (TFEL) displays. These displays need a luminescent layer which is sandwiched between dielectric and conductive layers. This application is demanding since low process temperatures have to be used because of the soda lime glass substrates. In addition large substrate sizes are needed and no pinholes are accepted. Suntola *et al.* were able to grow polycrystalline luminescent ZnS:Mn films and amorphous Al_2O_3 films by dosing sequentially the precursors. The quality of the ALE grown TFEL devices is high [38] and the method is industrially used in the production of monochrome and multicolor TFEL devices [39,40].

Worldwidely the studies on ALE are mainly focused on the growth of epitaxial III-V thin films giving emphasis on the self-limiting mechanisms in the growth of GaAs using trimethyl gallium [41,42]. The research activity in other areas has been amazingly low despite the fact that the only industrial applications have been in display devices where polycrystalline II-VI compounds and amorphous oxides are utilized. During the last years some increase in the activity in this sector can be recognized.

A new extension of the ALE method is its use in deposition on porous, high-surface-area substrates (silica, alumina) used as catalyst supports [43]. The basic work in this field includes the deposition of different transition metal oxides.

3. THERMODYNAMIC CONSIDERATIONS

In studying the deposition of thin films using new precursor - film material combinations thermodynamic considerations of the reactions prior to experimental work are useful. By calculating ΔG it is possible to predict the most feasible reaction. Unlike in CVD, where reactions with negative but close to zero ΔG are preferred to avoid uncontrolled gas phase reactions, in ALE the reactions should possess as negative ΔG values as possible, *i.e.* the precursors should react aggressively with each other. The high reactivity facilitates a use of short cycle times and a material efficient production of films with high purity. However, the final answer whether the film growth is taking place or not cannot be achieved only by the thermodynamic considerations for a few reasons. First the thermodynamic data available is limited to rather simple molecules and inorganic compounds. The HSC program by Outokumpu [44] we utilize contains data for 7708 species. The lack of data for organometallics and volatile metal complexes containing organic ligands is a serious limitation. Secondly, the thermodynamic study of reactions require that the reactants encounter each other in the gas phase but in the ALE method the precursors are not simultaneously present in the gas phase. The precursors chemisorb on the surface and possibly decompose partially, *i.e.* release one or two ligands. The film formation reaction occurs between these surface species. Thermodynamic data for these surface species are of course not known. Thirdly the thermodynamic considerations tell nothing about the kinetics.

In spite of the limitations it is possible to exclude impossible reactions by the thermodynamic calculations and save time in experimental work. The calculations appeared to be very useful in choosing reactions for the deposition of metal nitride thin films from metal chlorides and ammonia at low temperatures (Fig. 2). In growth of transition metal nitrides (TiN, NbN) where reduction of the metal is necessary for the nitride formation thermodynamics assists in finding suitable reducer [45,46] which in this case is metallic zinc. Hydrogen does not assist in reducing these metal chlorides

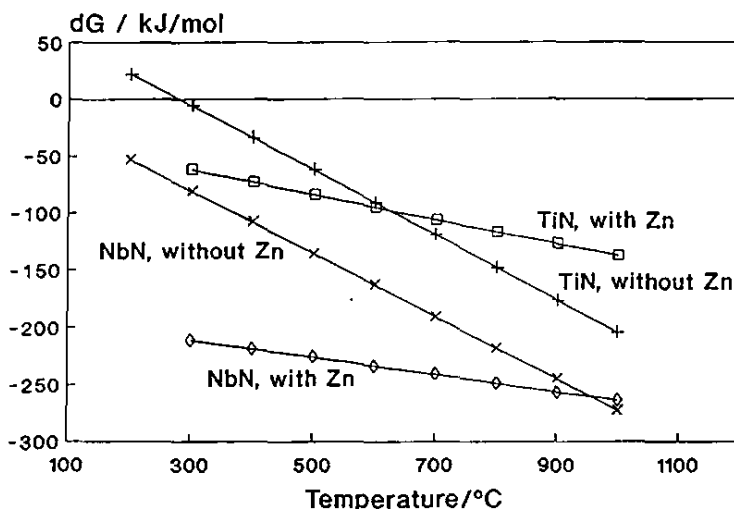


Figure 2: Gibbs energy vs. temperature for the growth reactions of TiN and NbN with and without Zn [44].

TiN without Zn: $\text{TiCl}_4(\text{g}) + 2 \text{NH}_3(\text{g}) = \text{TiN}(\text{s}) + 4 \text{HCl}(\text{g}) + \text{H}_2(\text{g}) + 0.5 \text{N}_2(\text{g})$

TiN with Zn: $\text{TiCl}_4(\text{g}) + \text{NH}_3(\text{g}) + 0.5 \text{Zn}(\text{g}) = \text{TiN}(\text{s}) + 3 \text{HCl}(\text{g}) + 0.5 \text{ZnCl}_2(\text{g})$

NbN without Zn: $\text{NbCl}_5(\text{g}) + 5/3 \text{NH}_3(\text{g}) = \text{NbN}(\text{s}) + 5 \text{HCl}(\text{g}) + 1/3 \text{N}_2(\text{g})$

NbN with Zn: $\text{NbCl}_5(\text{g}) + \text{NH}_3(\text{g}) + \text{Zn}(\text{g}) = \text{NbN}(\text{s}) + 3 \text{HCl}(\text{g}) + \text{ZnCl}_2(\text{g})$

from their higher oxidation states to +III; the direct reactions with NH_3 are more feasible than those where also hydrogen is involved.

Thermodynamic calculations may also help in understanding and interpreting poor and negative results obtained in deposition experiments. That was the case in our studies on the ALE deposition of Nb_2O_5 films from NbCl_5 and water where the process was irreproducible and resulted in films with severe thickness non-uniformities [45]. On the basis of thermodynamic calculations the results could be rationalized by the formation of stable NbOCl_3 and NbO_2Cl compounds. Especially the volatile NbOCl_3 can lead to etching of Nb_2O_5 .

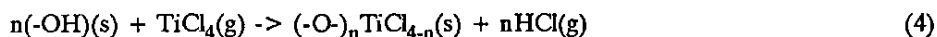
4. OXIDE THIN FILMS

The deposition of oxides was one of the first experiments made by ALE in 70s [37]. These oxides were aimed for dielectric films in TFEL devices. During the last 15 years several oxide thin films including MgO , ZnO , TiO_2 , ZrO_2 , HfO_2 , SnO_2 , CeO_2 , Al_2O_3 , In_2O_3 , Ta_2O_5 , Y_2O_3 , BaTiO_3 and MgAl_2O_4 have been deposited by ALE as reviewed by Ritala [20].

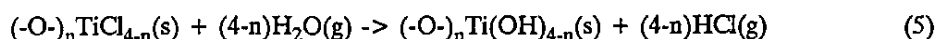
4.1 Deposition chemistry

Metal chlorides and water have most often been used as precursors in ALE deposition of oxide films. The chlorides are often good precursors because they are stable, volatile enough, reactive, cheap and not too difficult to handle [15]. The drawbacks of metal chlorides are that they in some cases (NbCl_5 , TaCl_5) may etch the film leading to a very slow growth rate of the oxide [45,47] or the reaction from chloride to oxide is not thermodynamically favored (ZnCl_2 , InCl_3). Alternative precursors are different organometallic compounds (methyl-, ethyl-, cyclopentadienyl compounds) [48-50], alkoxides [51-53] and β -diketonates [54,55]. Water is suitable oxygen source if metal chlorides [36,56-58] or alkyl precursors are used [50,59,60] but water is not necessarily the best choice to be used in combination with β -diketonates. Other possible oxygen sources are O_2 [61], H_2O_2 [48], alcohols [51], O_3 [54,55] and N_2O [62].

The most intensively studied ALE oxides are Al_2O_3 and TiO_2 . These both oxides have been deposited from different precursors: chlorides, alkoxides and Al_2O_3 from aluminium alkyls. The net reactions between metal chlorides and water are simple but the mechanisms of the surface reactions leading to the formation of oxide film may be complex [20,57]. The essential question in the interpretation of the mechanisms is if the surface is hydroxyl terminated or not after the water pulse. If the surface contains hydroxyl groups they are the places with which the metal chloride is reacting. In the case of TiCl_4 we can write:



where n is 1-3 mostly depending on the temperature and spatial distribution of the hydroxyls. The successive water pulse changes the surface back to a hydroxylated one:

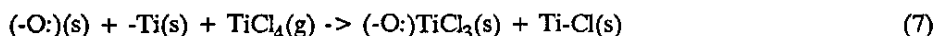


There is a possibility, however, that TiCl_4 reacts with the OH-groups in a way that volatile transient species $\text{Ti}(\text{OH})_{4-x}\text{Cl}_x$ are formed and this complicates the situation since $\text{Ti}(\text{OH})_{4-x}\text{Cl}_x$ may further react with the surface hydroxyls or decompose to TiO_2 or TiOCl_2 [63,64]. On the other hand, HCl

which is released in reactions 4 and 5 has a possibility to readsorb interacting either with the hydroxyl groups or oxygen bridges [20,65]. When readsorbed, HCl blocks the adsorption sites thereby lowering the growth rate. The growth mechanism (reactions 4 and 5) is supported by the mass spectrometric studies which showed both in the case of Al and Ti oxide that HCl is released both after the metal chloride and water pulses [66]. Furthermore, the amount of HCl after the TiCl_4 pulse was lower than expected suggesting that the readsorption of HCl does play a role. The other possibility is that the surface becomes dehydroxylated after the water pulse. In that case TiCl_4 would adsorb molecularly:



or dissociatively



The subsequent water pulse converts the surface to oxide and liberates HCl. Also here during the water pulse the formation of volatile transient $\text{Ti}(\text{OH})_{4-x}\text{Cl}_x$ molecules is possible. Thus the weak HCl signal after the TiCl_4 pulse in mass spectrometry may also indicate that at least partial dehydroxylation takes place at the temperatures (around 500 °C) usually used in the ALE growth of oxides from chlorides and water.

The growth rates observed in chloride processes carried out at 500 °C are 0.6 Å/cycle for Al_2O_3 [51,56], around 0.5 Å/cycle for TiO_2 [57], ZrO_2 [58] and HfO_2 [67], 0.43 Å/cycle for Ta_2O_5 [24], 0.27 Å/cycle for In_2O_3 [68] and 0.34 Å/cycle for SnO_2 [69]. The results show that only a submonolayer is growing during one cycle. The obvious reason for the low growth rate is the steric hindrance caused by the chloro ligands. The other reasons maybe the dehydroxylation which limits the number of reaction sites available, the formation of volatile hydroxide chloride species and the readsorption of HCl. It is worth noticing that the growth rate seems to be higher (> 1 Å/cycle) at lower temperatures (150-200 °C) [24,51,56] because of the larger amount of hydroxyl groups at the surface. At low temperatures, however, the contents of chloride and hydroxide residues in the films may be high weakening the film properties which can be seen in the refractive index values and etching properties.

Also in the reaction between metal alkyls and water the hydroxyl groups evidently play an important role. The lack of chloride ions makes the reaction simpler and high growth rates (> 1 Å/cycle) and uniform, thickness profile-free oxide films have been obtained by employing metal alkyl precursors [50,59,60].

The effect of the source chemical on the growth reaction has been studied in the case of Al, Ti and Ta oxides using alkoxides as alternative precursors [51-53,70]. Water served also here as an oxygen source. The alkoxides are common precursors in CVD because they can decompose to oxides. In ALE process the competing decomposition process has to be taken into account and this limits the process temperatures below 400 °C. If the growth is taking place in an ALE mode, i.e. if not significant self-decomposition is happening, the growth mechanism is the same as in the case of chlorides. This means that the reaction proceeds via hydroxylated surfaces and alcohols are liberated in the reactions. The size of the precursor molecule was found to affect the growth rate, i.e. the larger the molecule the lower the growth rate: with $\text{Ti}(\text{OCH}_2\text{CH}_3)_4$ 0.35 Å/cycle [53] and with $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$ 0.30 Å/cycle [52]. The exchange reaction with water was faster with the isopropoxide, saturating within 0.6 s at 250 °C, than with the ethoxide (1.5 s) indicating the difference in shielding of the metal ions in these alkoxides.

The crystalline outcome of the oxide films is dependent on several factors like the film material itself, substrate material, film thickness, growth temperature and precursors employed. When deposited on glass some of the ALE oxides (Al_2O_3 [51,56], Ta_2O_5 [70,71]) are completely amorphous to XRD while some others (e.g. HfO_2 [67], In_2O_3 [68]) possess highly oriented crystalline structures. On the other hand, the substrate material was found to have a significant effect on the crystallinity of the TiO_2 films grown from TiCl_4 and water [57]. Films having their thicknesses below 200 nm were essentially amorphous when deposited on amorphous substrates whereas those on crystalline substrates were more crystalline. However, when the film thickness was increased further also those TiO_2 films which were grown on glass exhibited increasing tendency towards crystallization [72]. This implies that an amorphous or poorly crystalline layer is first formed on the surface of the amorphous substrate and only subsequently the growth of crystalline material becomes favorable. In fact such a starting layer, though thinner than 40 nm, was found to precede also the deposition of the strongly oriented crystalline HfO_2 [67]. Electron diffraction studies, in turn, have revealed that the crystallization of TiO_2 and the formation of its different polymorphic phases are mainly dependent on substrate temperature [23]. The effect of the source material on the crystallinity of TiO_2 films is illustrated in Fig. 3. By contrast to the essentially amorphous film obtained from TiCl_4 at 500 °C [57], the films deposited from the alkoxides are more crystalline despite the fact they were grown below 350 °C [52,53]. This difference is attributed to the oligomerization of the alkoxides. By bridging between Ti ions at the surface, the alkoxide groups may form a constructive intermediate between an irregular adsorption layer and a crystalline film.

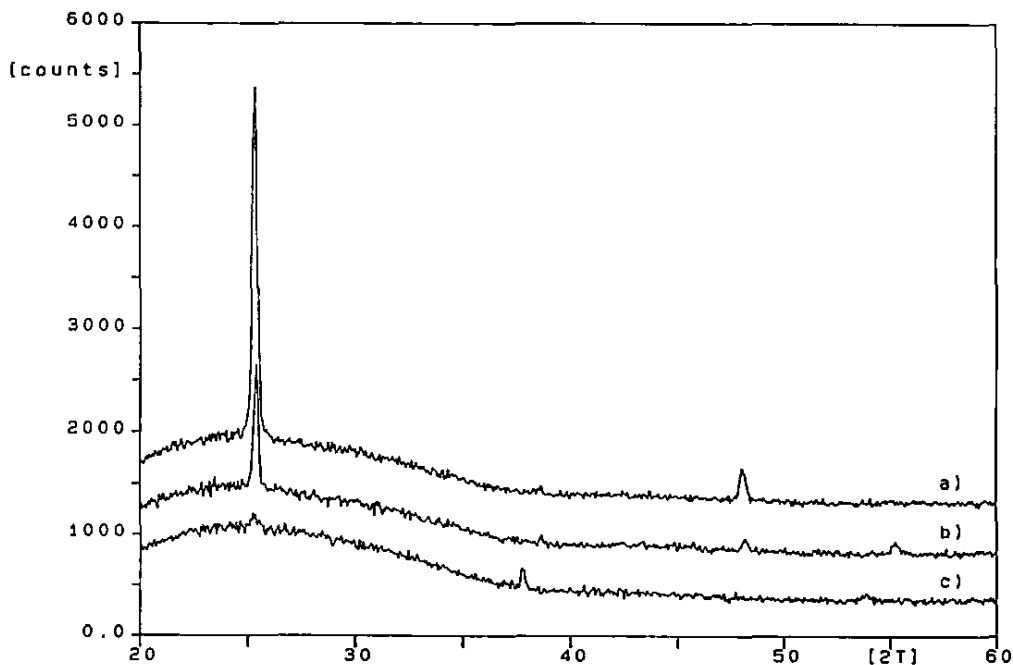


Figure 3: XRD patterns of 120 nm thick TiO_2 films grown on soda lime glass substrates from (a) titanium tetraisopropoxide at 325 °C, (b) titanium tetraethoxide at 250 °C and (c) TiCl_4 at 500 °C. In all the cases the other precursor was water.

4.2 Dielectric oxides

Al_2O_3 was the first dielectric oxide deposited by ALE and it was aimed for dielectric layers in TFEL devices [37]. The main purpose of the insulator is to protect the phosphor layer from a dielectric breakdown. Accordingly, insulators must have high resistivity, dielectric strength and capacitance. Other important properties of the insulator layer are of course good adhesion, chemical stability, small number of pinholes, high charge storage density and small dielectric loss [38,73]. ALE deposited Al_2O_3 films fulfil the demands of TFEL devices: dielectric constant = 8.3, breakdown voltage $> 10^6$ V/cm and they are pinhole free [71].

The electric properties, viz. losses and toleration of electric field, of Al_2O_3 films can be improved by doping it with TiO_2 . In commercial TFEL displays fabricated by ALE at least one of the dielectric layers is $\text{Al}_x\text{Ti}_y\text{O}_z$ [74].

Tantalum oxide has also been used in the early stage ALE TFEL devices as a dielectric layer [75]. Ta_2O_5 has higher dielectric constant (23-25) than Al_2O_3 but when the dielectric constant increases the leakage current tends to increase simultaneously [71]. Dielectric losses in ALE grown Ta_2O_5 films are in the order of 10^{-2} but the leakage current is significant in oxides prepared from chloride and still 2.3-4.0 mA/cm² at 1 MV/cm in those prepared from ethoxide [70,71]. The leakage current can be reduced by several orders of magnitude by introducing thin layers of another oxide to Ta_2O_5 , i.e. by composite films. So far the systems Ta_2O_5 - Al_2O_3 , Ta_2O_5 - HfO_2 and Ta_2O_5 - ZrO_2 have been studied and they show how the ALE method enables, besides decreasing the leakage current, also tailoring of dielectric constant and refractive index with the aid of multilayer structures [71,76,77].

4.3 Conducting oxides

Conducting oxides deposited by ALE include In_2O_3 , In_2O_3 :Sn (ITO), SnO_2 , SnO_2 :Sb, ZnO and ZnO:Al.

Polycrystalline In_2O_3 films with low resistivity and high transparency were deposited from InCl_3 and water at 500 °C [68]. This process suffered, however, from low growth rate (0.27 Å/cycle) which was related to an etching tendency of InCl_3 and its decomposition products. The resistivities of the films were in the order of 3×10^{-3} Ωcm. The doping of the In_2O_3 films by tin decreased further the growth rate to 0.20 Å/cycle. Two different doping schemes were employed, viz. giving one SnCl_4 pulse at a time, $(\text{In-O})_{49}/(\text{Sn-O})_1/(\text{In-O})_{49}$... or giving several successive SnCl_4 pulses, $(\text{In-O})_{98}/(\text{Sn-O})_2/(\text{In-O})_{98}$... The first pulsing scheme resulted in a higher Sn content of the films. Resistivities in the best ITO films were 2×10^{-4} Ωcm, while the carrier concentration was 6.3×10^{20} cm⁻³ and Hall mobility 45 cm²V⁻¹s⁻¹ [78,79]. The applicability of ALE ITO thin films to a-Si:H solar cells has been demonstrated [80]. In addition, the use of ALE grown ITO- TiO_2 film pairs in galvanic cells containing AlOOH as a solid electrolyte has been studied [81].

Tetragonal rutile-type SnO_2 was growing in the reaction between SnCl_4 and water at 300-600 °C [69]. The films were nearly stoichiometric, transparent and highly uniform and the maximum growth rate was 0.34 Å/cycle. The resistivity values (0.06-0.20 Ωcm) increased with increasing film thickness. The values are somewhat higher than usual in SnO_2 but typical to those prepared from chloride. Antimony doping of SnO_2 did not disturb the growth rate but lowered the resistivity to 1×10^{-3} Ωcm when one SbCl_5 pulse was given after each 75 SnCl_4 and water pulses [82]. Simultaneously the electron concentration increased from 1.9×10^{19} cm⁻³ to 7.2×10^{20} cm⁻³ and the maximum Hall mobility was 27.5 cm²V⁻¹s⁻¹. The adverse effect of the Sb doping was the decrease of transparency.

ZnO and Al doped ZnO thin films have successfully been deposited with ALE from the corresponding methyl or ethyl compounds and water [50]. The effect of steric hindrance on the

growth rate can nicely be seen by comparing the rates obtained with dimethyl zinc ($1.8 \text{ \AA/cycle}$ at 200°C) and diethyl zinc ($1.4 \text{ \AA/cycle}$). The resistivities were in the order of $8.9 \times 10^{-4} \Omega\text{cm}$ (sheet resistance $10 \Omega/\square$) in the films where 3 % of the Zn pulses were replaced by TMA pulses.

4.4 Ternary oxides

The growth of ternary oxides by ALE is a challenge because the achievement of correct stoichiometry is much more difficult than in the binary compounds. Oxide superconductors as quaternary compounds represent even more difficult case and no layer-by-layer ALE growth of, for example, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ where the superconducting phase would have been formed *in situ* has been carried out [10].

Few reports on attempts towards an ALE growth of ternary oxide films exist, however. Huang and Kitai [49] grew polycrystalline MgO films from bis(cyclopentadienyl)magnesium and water at $400\text{--}900^\circ\text{C}$ and amorphous Al_2O_3 from triethylaluminium and water. Ternary MgAl_2O_4 compound was prepared by pulsing the precursors in a sequence corresponding to the stoichiometry. The resulting films were amorphous and the existence of Mg and Al in the films was confirmed by Auger measurements.

BaTiO_3 thin films aimed for EL applications were grown from Ba β -diketonate, Ti iso-propoxide and N_2O on ITO covered glass substrates at 450°C [62]. The film obtained was amorphous and contained Ba, Ti and O as the main components as studied by Auger spectroscopy. The dielectric constant of the film was 19 and the charge storage capacity was $4.2 \mu\text{C}/\text{cm}^2$.

5. NITRIDE THIN FILMS

In CVD deposition of metal nitrides the most common precursors are metal chlorides with either N_2 and H_2 or with ammonia [3]. Temperatures below 500°C are difficult to achieve with these reactions because of the high chlorine contamination which weakens the film properties [83-87]. Low temperature CVD processes are possible but they require different precursors like metalorganic compounds (alkylamides [88,89], metal alkyl or cyclopentadienyl compounds [86]) and methylhydrazine or tert-butylamine as nitrogen precursors [87] or the use of plasma [90] or hot filament activated [91] processes. In CVD the pyrolysis of complexes containing the metal-nitrogen bond have been used in low-temperature deposition of nitride films [92] but this process may also yield TiCN films [93].

Metal (Al, In, Ti, Nb, Ta, Mo) nitride films can be deposited by ALE from metal chlorides and ammonia at 500°C [45,46,94-96]. The resulting films are pure and the chlorine content is low - not detectable with RBS and XRF in the case of transition metal nitrides and 3 at-% in the case of AlN. If the growth temperature in the case of TiN is lowered to 400°C the chlorine content increases and the film properties change accordingly. The growth rate in the case of transition metal nitrides is low, around $0.2 \text{ \AA/cycle}$ but with AlN it is $1 \text{ \AA/cycle}$. The reaction $\text{MCl}_x (x>3) + \text{NH}_3$ is not very favorable at these temperatures and additional reduction to M^{III} is needed.

To obtain uniform transition metal nitrides with low resistivity a reducing Zn intermediate pulse can be used between the metal chloride and NH_3 pulses [45,46,97]. The metallic zinc reduces the surface metal species and forms gaseous ZnCl_2 which is purged out. No zinc is remaining in the film. The use of zinc affects the visual appearance of the films, improves their conductivity but does not increase the growth rate. The lowest resistivity measured for TiN films grown with Zn at 500°C was $50 \mu\Omega\text{cm}$ [46].

The nitride films (AlN, TiN) may contain some oxygen and there can be an oxygen profile in the flow direction so that the maximum amount is observed at the leading edge of the substrate. AlN seems to oxidize very easily and the origin of the oxygen may be the nitrogen carrier gas and/or ammonia [95]. The origin of oxygen in TiN was attributed to post depositional oxidation because the oxygen content was lowest in the thickest films. Oxygen is probably located at the surfaces of the grains thus explaining why its relative amount decreases in thicker films where the surface to bulk ratio is smaller. The intermediate Zn pulse reduced slightly the oxygen content [46].

NbCl₅ is still a special case because of its strong etching tendency which further lowers the growth rate. By keeping the pulse time of NbCl₅ as short as 0.1 s and lengthening the NH₃ pulse to 1.0 s a rate of 0.25 Å/cycle could be obtained [45].

Metal alkyl compounds are alternative precursors also in the ALE deposition of nitrides as shown by Mayer *et al.* [98] who used trimethyl aluminium and ammonia and Asif Khan *et al.* [99-102] who used triethyl aluminium, triethyl gallium and ammonia in deposition of GaN and AlN thin films and their superlattices. Smooth, epitaxial nitride film could be deposited on a single crystal substrate already at 450 ° which is 250 °C lower than that used in a conventional low-pressure CVD. Plasma-enhanced ALE has been employed in depositing both single crystal and polycrystalline GaN films from trimethyl gallium and N+H plasma on sapphire with different orientations [103]. The substrate surface treatment strongly affected the quality of the film grown.

6. FILM MORPHOLOGY

The oxide and nitride films deposited by ALE have been uniform, dense and free of any significant contamination. Their characterization by scanning electron microscopy (SEM) and atomic force microscopy (AFM) have revealed interesting results from the evolution of the surface morphology during the film growth. It was found that the materials grown on glass can be divided in two groups: amorphous with smooth surfaces and polycrystalline with roughened surfaces. Typical totally amorphous materials are Al and Ta oxides. The reason to this may be in the surface mobility or in the growth reaction. Both the SEM and AFM measurements show that these oxide films are extremely flat and homogeneous [70,104]. The surface roughness of a 800 nm thick Al₂O₃ films is only about 2 nm.

In polycrystalline films the surface roughness increases with the film thickness which is in an obvious contradiction with the ideal layer-by-layer growth mechanism. The agglomeration starts immediately at the beginning of the film growth [105]. Because the gas-phase reactions can be neglected, the obvious reasons for the agglomeration are the surface migration processes driven by the free-energy associated with the film-substrate interface. In metal chloride - water processes the migration of hydroxyl groups and hydroxide chloride intermediate species may be responsible for the agglomeration and surface roughening. Support to this statement is obtained from the experiments made with TiCl₄ and water to deposit TiO₂ on amorphous silica powder. In that case strong agglomeration and crystalline TiO₂ was detected by XRD even after one reaction cycle and without the water pulse [64,106,107]. The apparent consequence of the surface roughening is that when the film becomes thicker and rougher light scattering from its surface becomes significant leading to a milky appearance and reduced specular transparency. In TiO₂ films grown by ALE at 500 °C, for example, the light scattering is already significant for films with thicknesses of the order of 400 nm. Besides film thickness also other factors like precursors used, growth temperature and substrate material may affect the surface roughening.

Roughening of TiO₂ films could be reduced by intermediate Al₂O₃ layers [72]. The Al₂O₃ layers prevented the growth of the TiO₂ agglomerates and the TiO₂ layers had to rebegin the nucleation

after each aluminium oxide layer. Films which consisted of 20 pairs of $\text{TiO}_2\text{-Al}_2\text{O}_3$ layers where each pair further consisted of 900 Ti-O and 100 Al-O cycles, were 850 nm thick, highly transparent and had surface roughness of 8.2 nm to be compared with a roughness of 25 nm measured for a pure TiO_2 film with a comparable thickness. The cross-sectional SEM micrographs proved also that the particles in the films containing the intermediate Al_2O_3 layers are significantly smaller than those found in pure TiO_2 films.

7. CONCLUSIONS

ALE is a competitive and versatile method to grow oxide and nitride thin films on large area substrates. The reviewed papers show that uniform dielectric and conductive oxide as well as nitride thin films have been deposited by ALE. The applicability of ALE to an industrial scale is evidenced by its use in fabrication of TFEL displays.

The principle of the ALE method is simple: alternate reactions via saturated surfaces. However, the deeper study of the reaction mechanisms shows the complexity of the process. The full understanding of the growth of e.g. oxide films is not possible by analyzing only the resulting films and growth rates. AFM/STM methods have revealed new information on the growth mechanisms but still *in situ* monitoring of the reactions is greatly needed to gain a detailed insight into the growth reactions and, thereby, to improve the process control and to assist in designing new ALE processes.

References

- [1] Venkatesan, T., *Thin Solid Films* **216** (1992) 52-58.
- [2] Sneh, O., Wise, M.L., Okada, L.A., Ott, A.W. and George, S.M., *Mat. Res. Soc. Symp. Proc.* **334** (1994) 25-30.
- [3] Pierson, H.O., *Handbook of Chemical Vapor Deposition (CVD)* (Noyes Publications, Park Ridge, N.J. 1992) pp. 226-242.
- [4] Sze, S.M., *Semiconductor Devices, Physics and Technology* (John Wiley & Sons, New York, 1985).
- [5] Singer, P., *Semicond. Int.* Sept. (1992) 32.
- [6] Bange, K. and Gambke, T., *Adv. Mater.* **2** (1990) 10-16.
- [7] Bauer, G. H., *Appl. Surf. Sci.* **70/71** (1993) 650-659.
- [8] Chopra, K.L., Major, S. and Pandya, K.D., *Thin Solid Films* **102** (1983) 1-46.
- [9] Leskelä, M.A., Truman, K.J., Mueller, C.H. and Holloway, P.H., *J. Vac. Sci. Technol. A* **7** (1989) 3147-3171.
- [10] Leskelä, M., Mölsä, H. and Niinistö, L., *Supercond. Sci. Technol.* **6** (1993) 627-656.
- [11] Strite, S. and Morkoc, H., *J. Vac. Sci. Technol. B* **10** (1992) 1237-1266.
- [12] Shintani, A. and Minagawa, S., *J. Electrochem. Soc.* **123** (1976) 1725-1729.
- [13] Chatterjee, S., Chandrashekhar, S. and Sudarshan, T.S., *J. Mater. Sci.* **27** (1992) 3409-3423.
- [14] Travis, E.O. and Fiordilace, R.W., *Thin Solid Films* **236** (1993) 325-329.
- [15] Leskelä, M. and Niinistö, L., in *Atomic Layer Epitaxy*. Suntola, T. and Simpson, M. (Eds.) (Blackie and Son Ltd, Glasgow 1990) pp. 1-39.
- [16] Pakkanen, T.A., Nevalainen, V., Lindblad, M. and Makkonen, P., *Surf. Sci.* **188** (1987) 456-474.
- [17] Rautanen, J., Leskelä, M., Niinistö, L., Nykänen, E., Soininen, P. and Utriainen, M., *Appl. Surf.*

- Sci.* 82/83 (1994) 553-558.
- [18] Leskelä, M., *Acta Polytechn. Scand., Ser. Chem. Technol.* 195 (1990) 67-80.
 - [19] Suntola, T., *Thin Solid Films* 225 (1993) 96-98.
 - [20] Ritala, M., *Ann. Acad. Sci. Fenn. Ser. A II. Chemica* 257 (1994) 1-48.
 - [21] Huang, R. and Kitai, A.H., *J. Mater. Sci. Lett.* 12 (1993) 1444-1446.
 - [22] Ranta-aho, T. and Ylilammi, M., *J. Electrochem. Soc.* 141 (1994) 1278-1284.
 - [23] Aarik, J., Aidla, A., Uustare, T. and Sammelselg, V., *J. Cryst. Growth* 148 (1995) 268-275.
 - [24] Kukli, K., Aarik, J., Aidla, A., Kohan, O., Uustare, T. and Sammelselg, V., *Thin Solid Films*. In press.
 - [25] Goodman, C.H.L. and Pessa, M., *J. Appl. Phys.* 60 (1986) R65-R81.
 - [26] Yao, T. and Takeda, T., *Appl. Phys. Lett.* 48 (1986) 160-162.
 - [27] Nishizawa, J., Abe, H. and Kurabayashi, T., *J. Electrochem. Soc.* 132 (1985) 1197-1200.
 - [28] DenBaars, S.P., Beyler, C.A., Hariz, A., and Dapkus, P.D., *Appl. Phys. Lett.* 51 (1987) 1530-1532.
 - [29] Usui, A. and Sunakawa, H., *Jpn. J. Appl. Phys.* 25 (1986) L212-L214.
 - [30] Bedair, S.M., Tischler, M.A., Katsuyama, T. and El-Masry, N.A., *Appl. Phys. Lett.* 47 (1985) 51-53.
 - [31] Tischler, M.A. and Bedair, S.M., in *Atomic Layer Epitaxy*. Suntola, T. and Simpson, M. (Eds.), (Blackie and Son Ltd, Glasgow 1990) pp. 110-154.
 - [32] Doi, A., Aoyagi, Y. and Namba, S., *Appl. Phys. Lett.* 48 (1986) 1787-1789.
 - [33] Karam, N.H., Liu, H., Yoshida, I. and Bedair, S.M., *Appl. Phys. Lett.* 52 (1988) 1144-1146.
 - [34] Suntola, T. and Hyvärinen, J., *Annu. Rev. Mater. Sci.* 15 (1985) 177-195.
 - [35] Suntola, T., *Thin Solid Films* 216 (1992) 84-89.
 - [36] Suntola, T., Pakkala, A. and Lindfors, S., *U.S. Patent* 4,389,973 (1983).
 - [37] Suntola, T., Antson, J., Pakkala, A. and Lindfors, S., *SID 80 Digest* 11 (1980) 108-109.
 - [38] Sutela, T., *Display Technol. Appl.* 5 (1984) 73-78.
 - [39] Karila, J., Hyvärinen, J. and Törnqvist, R., *Conf. Proc. Eurodisplay 87*, Paris 1987, p. 236.
 - [40] Haaranen, J., Törnqvist, R., Koponen, J., Pitkänen, T., Surma-aho, M., Barrow, W. and Laakso, C., *SID 92 Digest* 23 (1992) 348-351.
 - [41] Proceedings of the 1st International Symposium on Atomic Layer Epitaxy, *Acta Polytechn. Scand., Ser. Chem. Technol.* 195 (1990) Niinistö, L. (Ed.); Proceedings of the 2nd International Symposium on Atomic Layer Epitaxy, *Thin Solid Films* 225 (1993) Bedair, S.M. (Ed.); Proceedings of the 3rd International Symposium on Atomic Layer Epitaxy, *Appl. Surf. Sci.* 82/83 (1994) Ozeki, M., Usui, A., Aoyagi, Y. and Nishizawa, J. (Eds.).
 - [42] Niinistö, L. and Leskelä, M., *Thin Solid Films* 225 (1993) 130-135.
 - [43] Lakomaa, E.-L., *Appl. Surf. Sci.* 75 (1994) 185-196.
 - [44] Outokumpu HSC Chemistry for Windows program package, Version 1.10 (Outokumpu Research Oy, Pori, Finland, 1993).
 - [45] Elers, K.-E., Ritala, M., Leskelä, M. and Rauhala, E., *Appl. Surf. Sci.* 82/83 (1994) 122-125.
 - [46] Ritala, M., Leskelä, M., Rauhala, E. and Haussalo, P., *J. Electrochem. Soc.* Submitted.
 - [47] Aarik, J., Aidla, A., Kukli, K. and Uustare, T., *J. Cryst. Growth* 144 (1994) 116-119.
 - [48] Fan, J.K., Sugioka, K. and Toyoda, K., *Mat. Res. Symp. Ser. Proc.* 222 (1991) 327-332.
 - [49] Huang, R. and Kitai, A.H., *J. Electron. Mater.* 22 (1993) 215-220.
 - [50] Lujala, V., Skarp, J., Tammenmaa, M. and Suntola, T., *Appl. Surf. Sci.* 82/83 (1994) 34-40.
 - [51] Hiltunen, L., Kattelus, H., Leskelä, M., Mäkelä, M., Niinistö, L., Nykänen, E., Soininen, P. and Tiitta, M., *Mater. Chem. Phys.* 28 (1991) 379-388.
 - [52] Ritala, M., Leskelä, M., Niinistö, L. and Haussalo, P., *Chem. Mater.* 5 (1993) 1174-1181.

- [53] Ritala, M., Leskelä, M. and Rauhala, E., *Chem. Mater.* **6** (1994) 556-561.
- [54] Mölsä, H., Niinistö, L. and Utriainen, M., *Adv. Mater. Optics Electronics* **4** (1994) 389-400.
- [55] Mölsä, H. and Niinistö, L., *Mat. Res. Soc. Symp. Proc.* **335** (1994) 341-350.
- [56] Aarik, J., Aidla, A., Jaek, A., Kiisler, A.-A. and Tammik, A.-A., *Acta Polytechn. Scand., Ser. Chem. Technol.* **195** (1990) 201-208.
- [57] Ritala, M., Leskelä, M., Nykänen, E., Soininen, P., and Niinistö, L., *Thin Solid Films* **225** (1993) 288-295.
- [58] Ritala, M. and Leskelä, M., *Appl. Surf. Sci.* **75** (1994) 333-340.
- [59] Higashi, G.S. and Fleming, C.G., *Appl. Phys. Lett.* **55** (1989) 1963-1965.
- [60] George, S.M., Sneh, O., Dillon, A.C., Wise, M.L., Ott, A.W., Okada, L.A. and Way, J.D., *Appl. Surf. Sci.* **82/83** (1994) 460-467.
- [61] Oya, G. and Sawada, Y., *J. Cryst. Growth* **99** (1990) 572-576.
- [62] Lee, D.H., Cho, Y.S., Lee, J.K. and Jung, H.J., *Mat. Res. Soc. Symp. Proc.* **310** (1993) 397-402.
- [63] Hair, M.L. and Hertl, W., *J. Phys. Chem.* **77** (1973) 2070-2075.
- [64] Haukka, S., Lakomaa, E.-L. and Root, A., *J. Phys. Chem.* **97** (1993) 5085-5094.
- [65] Parfitt, G.D., Ramsbotham, J. and Rochester, C.H., *Trans. Faraday Soc.* **67** (1971) 3100-3109.
- [66] Sonninen, M. and Hyvärinen, J., Unpublished results.
- [67] Ritala, M., Leskelä, M., Niinistö, L., Prohaska, T., Friedbacher, G. and Grasserbauer, M., *Thin Solid Films* **250** (1994) 72-80.
- [68] Asikainen, T., Ritala, M. and Leskelä, M., *J. Electrochem. Soc.* **141** (1994) 3210-3213.
- [69] Virola, H. and Niinistö, L., *Thin Solid Films* **249** (1994) 144-149.
- [70] Kukli, K., Ritala, M. and Leskelä, M., *J. Electrochem. Soc.* **142** (1995) 1670-1675.
- [71] Kattelus, H., Ylilammi, M., Saarihahti, J., Antson, J. and Lindfors, S., *Thin Solid Films* **225** (1993) 296-298.
- [72] Ritala, M., Leskelä, M., Niinistö, L., Prohaska, T., Friedbacher, G. and Grasserbauer, M., *Thin Solid Films* **249** (1994) 155-162.
- [73] Leskelä, M. and Tammenmaa, M., *Mater. Chem. Phys.* **16** (1987) 349-371.
- [74] Antson, H., Grasserbauer, M., Hamilo, M., Hiltunen, L., Koskinen, T., Leskelä, M., Niinistö, L., Stinger, G. and Tammenmaa, M., *Fresenius Z. Anal. Chem.* **322** (1985) 175-180.
- [75] Törnqvist, R. and Tuomi, T., *J. Lumin.* **24/25** (1981) 901-904.
- [76] Kattelus, H., Ylilammi, M., Salmi, J., Ranta-aho, T., Nykänen, E. and Suni, I., *Mat. Res. Soc. Symp. Proc.* **284** (1993) 511-516.
- [77] Kukli, K., Ihanus, J., Ritala, M. and Leskelä, M., To be published.
- [78] Asikainen, T., Ritala, M. and Leskelä, M., *Vacuum*. In press.
- [79] Asikainen, T., Ritala, M. and Leskelä, M., *J. Electrochem. Soc.* Submitted.
- [80] Ouwers, J.D., Schropp, R.E.I., Wallinga, J., van der Weg, W.F., Ritala, M., Leskelä, M. and Hyvärinen, J., *Proc. 12th Europ. Photov. Solar Energy Conf.* 1994 pp. 1296-1299.
- [81] Turković, A., Musić, S., Dragčević, D., Popović, S., Ritala, M., Asikainen, T. and Leskelä, M., Proceedings of the 8th CIMTEC Conference on Modern Materials & Technologies, Firenze 1994. In press.
- [82] Virola, H. and Niinistö, L., *Thin Solid Films* **251** (1994) 127-135.
- [83] Hegde, R.I., Fiordalice, R.W., Travis, E.O. and Tobin, P.J., *J. Vac. Sci. Technol. B* **11** (1993) 1287-1296.
- [84] Nickel, K., Riedel, R. and Petzow, G., *J. Amer. Ceram. Soc.* **72** (1989) 1804-1810.
- [85] Pierson, H.O., *J. Comp. Mater.* **9** (1975) 228-240.
- [86] Sherman, A., *Jpn. J. Appl. Phys.* **30** (1991) 3553-3557.
- [87] Price, J.B., Borland, J.O. and Selbrede, S., *Thin Solid Films* **236** (1993) 311-318.

- [88] Fix, R., Gordon, R.G. and Hoffman, D.M., *Chem. Mater.* **3** (1991) 1138-1148.
- [89] Dubois, L.H., *Polyhedron* **13** (1994) 1329-1336.
- [90] Akahori, T., Tanihara, A. and Tano, M., *Jpn. J. Appl. Phys.* **30** (1991) 3558-3561.
- [91] Deshpande, S.V. and Gulari, E., *Mat. Res. Soc. Symp. Proc.* **327** (1994) 115-120.
- [92] Ho, K., Annapragada, A. and Jensen, K., *Proc. 11th Int. Conf. on CVD*. Spear, K. and Cullen, G. (Eds.) (Electrochemical Society, Pennington NJ 1990) pp. 388-394.
- [93] Eizenberg, M., Littau, K., Ghanayem, S., Mak, A., Maeda, Y., Chang, M. and Sinha, S.K., *Appl. Phys. Lett.* **65** (1994) 2416-2418.
- [94] Higuchi, K., Unno, A. and Shiraishi, T., *Mat. Res. Soc. Symp. Proc.* **222** (1991) 169-173.
- [95] Eilers, K.-E., Ritala, M., Johansson, L.-S. and Leskelä, M., *J. Phys. IV* This issue.
- [96] Hiltunen, L., Leskelä, M., Mäkelä, M., Niinistö, L., Nykänen, E. and Soininen, P., *Thin Solid Films* **166** (1988) 149-154.
- [97] Nykänen, E., Mäkelä, M., Soininen, P., Leskelä, M. and Niinistö, L., to be published.
- [98] Mayer, T.M., Rogers Jr., J.W. and Michalske, T.A., *Chem. Mater.* **3** (1991) 641-646.
- [99] Asif Khan, M., Skogman, R.A., Van Hove, J.M., Olson, D.T. and Kuznia, J.N., *Appl. Phys. Lett.* **60** (1992) 1366-1368.
- [100] Asif Khan, M., Kuznia, J.N., Olson, D.T., Van Hove, J.M., Blasingame, M. and Reitz, L.F., *Appl. Phys. Lett.* **60** (1992) 2917-2919.
- [101] Asif Khan, M., Kuznia, J.N., Skogman, R.A., Olson, D.T., MacMillan, M. and Choyke, W.J., *Appl. Phys. Lett.* **61** (1992) 2539-2541.
- [102] Asif Khan, M., Kuznia, J.N., Olson, D.T., George, T. and Pike, W.T., *Appl. Phys. Lett.* **63** (1993) 3470-3472.
- [103] Hwang, C.-Y., Lu, P., Mayo, W.E., Lu, Y. and Liu, H., *Mat. Res. Soc. Symp. Proc.* **326** (1994) 347-352.
- [104] Ritala, M., Saloniemi, H., Leskelä, M., Prohaska, T., Friedbacher, G. and Grasserbauer, M., *Thin Solid Films*. Submitted.
- [105] Ritala, M., Leskelä, M., Johansson, L.-S. and Niinistö, L., *Thin Solid Films* **228** (1993) 32-35.
- [106] Haukka, S., Lakomaa, E.-L., Jylhä, O., Vilhunen, J. and Hornytzkyj, S., *Langmuir* **9** (1993) 3497-3506.
- [107] Lakomaa, E.-L., Haukka, S. and Suntola, T., *Appl. Surf. Sci.* **60/61** (1992) 742-748.