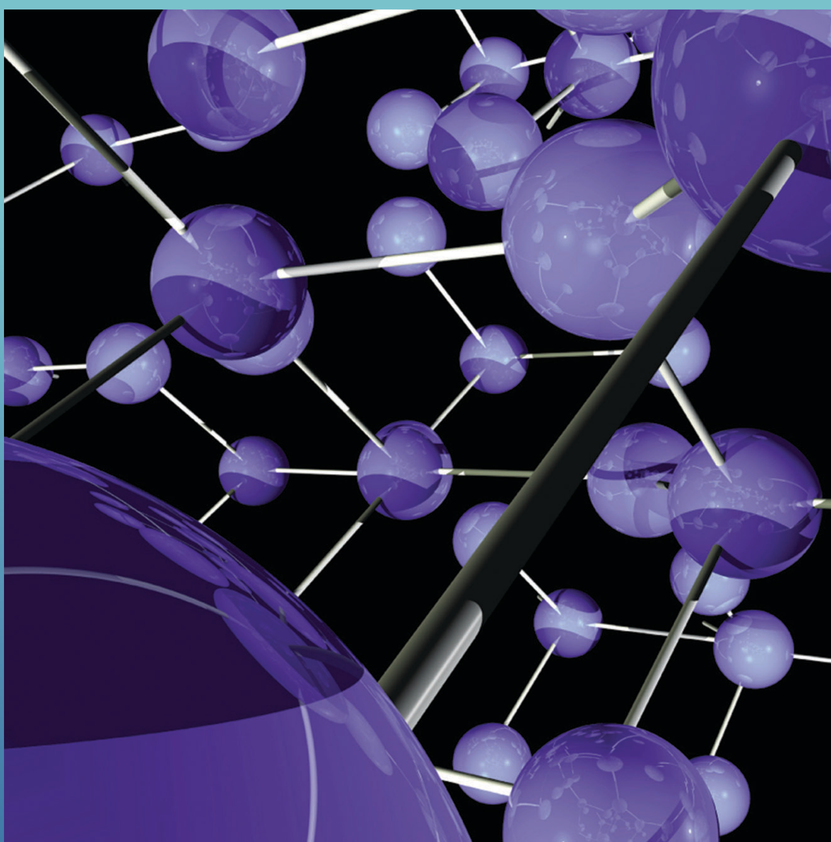
National Programme on Electronic Materials and Microsystems



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MICROELECTRONICS MATERIALS IN SCALED-DOWN SYSTEMS (MEMSS)

Jouni Ahopelto[1], Jukka Pekola[2], Päivi Törmä[2], Harri Lipsanen[3], Jukka Tulkki[4]

Abstract

In this project the properties of nanoscale semiconductor structures are investigated. The structures include silicon single electron tunneling devices, semiconductor-superconductor devices and 3-5 compound semiconductor structures. The single electron transistors fabricated on silicon on insulator substrates show Coulomb oscillations up to 100 K. Persistent current oscillations are observed in these devices at low temperatures after a gate voltage swing. The thermally activated behaviour of the oscillations suggests that shallow traps in the vicinity of the active part of the device are the origin of the oscillations. In the project also silicon-superconductor junctions are investigated. The junctions are used to probe directly the temperature of electrons in silicon. The thermal resistance between electrons and phonons and the thermal conductivity of electrons in degenerate silicon films is measured. Novel semiconductor-superconductor microcoolers are realized on silicon on insulator substrates. The devices show efficient cooling of electrons in silicon at sub-Kelvin temperatures. The possibility to integrate compound semiconductor emitters with polysilicon waveguides is investigated. Indium gallium arsenide quantum dots and wells buried in gallium arsenide grown on top of silicon have potential as integrated emitters on low cost silicon waveguides. Calculations of the transport properties of narrow silicon channels are performed, taking into account the effect of oxide induced strain on the potential landscape. The new results obtained and the new devices realized in this project show that there are still many unexplored areas in the field of semiconductor nanoelectronics.

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1 Partners and Funding

1.1 VTT Centre for Microelectronics

The research group (hereafter VTT) consists of subproject leader Research Professor Jouni Ahopelto, graduate students Mika Prunnila and Tomi Haatainen and student Eeva-Riitta Havukainen. Main part of the processing has been carried out by clean room operators.

1.2 Department of Physics, University of Jyväskylä

The research group (hereafter JyU) consists of subproject leaders Jukka Pekola and Päivi Törmä, senior researchers Antti Manninen, Klavs Hansen and Alexander Savin, postgraduate students Pasi Kivinen, Mikko Leivo, Anssi Lindell and Jussi Toppari, students Jari Kauranen, Riku Lassila, Jukka Mattila, Tomi Ryynänen, Turkka Salminen and Tarmo Suppula, and one technician Markku Särkkä. People who have been payed (totally or partly) from this Academy of Finland project are: Alexander Savin, Klavs Hansen, Jari Kauranen, Riku Lassila, Turkka Salminen, Tarmo Suppula and Markku Särkkä.

1.3 Optoelectronics Laboratory, Helsinki University of Technology

The research group (hereafter OL) consists of subproject leader Professor Harri Lipsanen and graduate students Juha Riikonen and Juha Toivonen.

1.4 Laboratory of Computational Engineering, Helsinki University of Technology

The research group (hereafter LCE) consists of subproject leader Professor Jukka Tulkki, postgraduate students Fredrik Boxberg, Jani Oksanen and Roman Terechonkov and student Kari Maijala.

1.5 Funding

Table 1. Funding of the project in 1000 FIM in 1999-2002. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1999	2000	2001	2002	**Total**
VTT	VTT	71	151	807	514	**1543**
	Academy	169	334	353	244	**1100**
JyU	JyU	410	485	365	221	**1481**
	Academy	159	310	310	221	**1000**
	ESA	180	250	90	40	**560**
OL	HUT	40	70	70	50	**230**
	Academy	60	180	180	80	**500**
LCE	HUT	100	100	100	100	**400**
	Academy	100	200	200	100	**600**
Total		**1289**	**2080**	**2475**	**1570**	**7414**

2 Research Work

2.1 Objectives and Work Plan

The aim in the project was to study the physical mechanisms that govern the performance of nanoscale transport devices, such as quantum point contacts (QPC) and single electron tunneling devices (SET). The devices were to be realized using three different material systems: silicon-on-insulator (SOI), SiGe and InGaAs/InP. In addition, structures utilizing self-organizing quantum dots were planned to be investigated. Modeling the strain effects and transport in the nanoscale devices was also included in the working plan. Because the eventual funding from the Academy was somewhat less than that we suggested in the original working plan for successful fulfillment of the tasks, the part dedicated for SiGe materials was removed from the final working plan.

In the during the project, a few new topics not mentioned in the original working plan emerged. One was the application of silicon-metal contacts as semiconductor-superconductor (Sm-S) tunneling junctions. In these contacts the Schottky barrier formed at the interface forms the tunneling barrier. Using the junctions cryogenic S-Sm-S microcoolers were realized for the first time. The barriers were also used to measure the electron gas temperature in silicon, and the electron-phonon thermal resistance could be deduced from experiments. The details are given in the next section.

Another new topic was the investigation of the possibility to integrate optically active 3-5 structures with silicon. The work was focused on the fabrication and materials research of novel GaAs-structures on polycrystalline silicon templates.

Regarding the modeling, one new topic emerged: modeling of self organized quantum wires in corrugated quantum wells grown on vicinal (111) surface in AlGaAs /InGaAs structures. This structure has strongly anisotropic conductance and optical emission, and 1D wires are naturally formed during the growth of the QW.

2.2 Progress Report: Common Themes

The working plan of the MEMSS consortium concentrated on fabrication and characterization of the properties of various nanoscale semiconductor structures. These included silicon single electron transistors, semiconductor-superconductor junctions and their application to electron thermometry and microcoolers, 3-5 heterostructures and 3-5 structures on silicon. The modeling concentrated on silicon point contacts and on strain created during thermal oxidation of nanoscale silicon structures.

Single electron transistor

Single electron tunneling devices are considered as potential building blocks for future micro and nanoelectronic circuits. Silicon is very promising material for nanotechnology due to the possibility to utilize standard Si technology. Silicon dioxide forms a high, stable tunneling barrier and thermal oxidation can be used to reduce of the final size of the structures. Silicon single electron transistors with side gates were fabricated on heavily doped SOI wafers. The devices were patterned using e-beam lithography (mainly at the University of Würzburg) and dry etching [1]. The final dimensions were achieved by thermal oxidation. The reproducibility was not very good. For example, the devices from the same processing batch showed different characteristics: most of the SETs seemed to have multiple dot array behavior at low temperature and only one showed single island behavior in a wide range of temperatures [3]. The I-V characteristics of all SETs investigated had clear Coulomb blockade region at temperatures up to 100 K and pronounced nonlinear behaviour even at 300 K. A set of I-V_g curves are shown in Fig. 1. At temperatures below 20 K, long term oscillations (relaxation) of source-drain current after switching on the gate voltage were observed in both multiple dot and single dot samples [36]. The oscillations vanished at temperatures above 20 K. Fig. 2 shows the behaviour at various temperatures. Furthermore, illumination of the SETs by red LED suppressed the relaxation process. The thermally activated behaviour of the oscillations, and also the effect of carrier generation by light, suggests that the

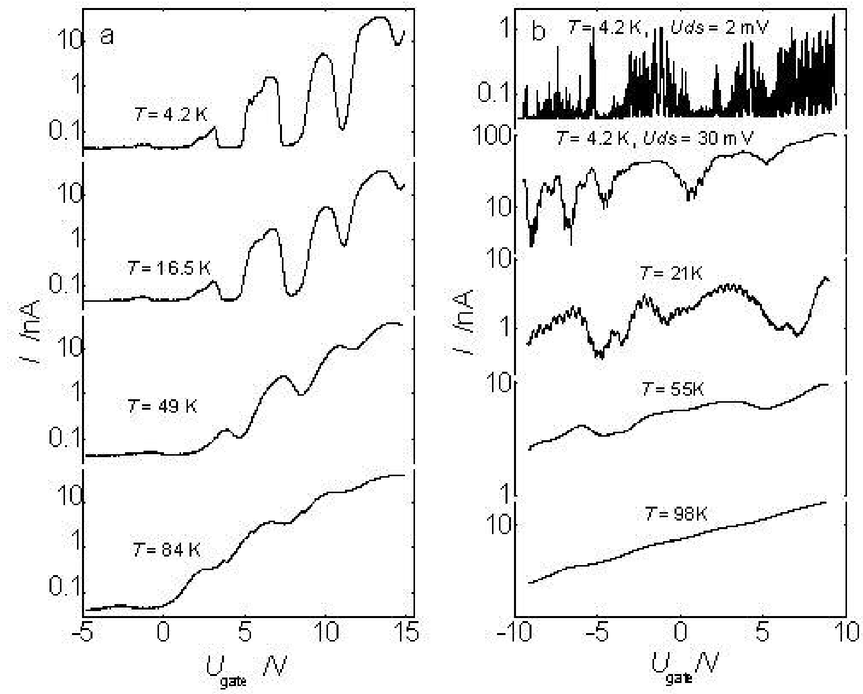

Fig. 1. Coulomb oscillations measured from two silicon SETs. The sample in (a) shows single dot and the sample in (b) multi dot behaviour. The oscillations sustain up to temperatures around 100 K.

origin of the oscillations are slowly saturating trap states in the vicinity of the channel of the SET. This work was carried out in collaboration between VTT and JyU.

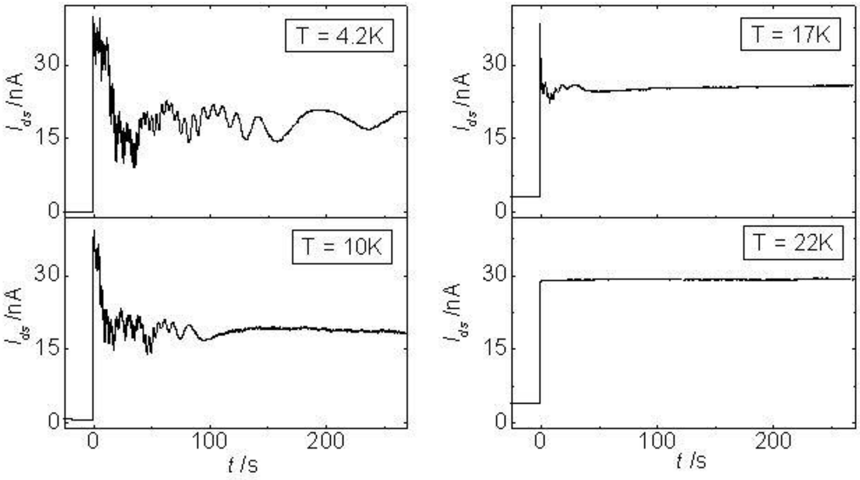

Fig. 2. Persistent current oscillations observed at low temperature after fast gate voltage swing.

Application of superconductor-semiconductor structures for thermometry and electronic cooling

One of the main directions of research during the last half in the project was the development of a new family of nanodevices based on quasiparticle tunneling in superconductor-semiconductor (S-Sm) junctions with Schottky barrier as the tunneling barrier (VTT and JyU). Here we have used degenerate thin SOI film as the semiconductor and mainly aluminum as the superconductor. Samples with niobium and molybdenum contacts were also fabricated. The possibility to use Sm-S structures to probe directly the temperature of the electron gas in Si at low temperature was demonstrated in the project [4]. The conductance of an Sm-S junction is very sensitive to the thermal distribution of electrons in the semiconductor. The junction can be used as thermometer after calibration against external thermometer in the sample holder. It was also found that Semiconductor – normal metal junction with Schottky barrier with high electric resistance can be used for on-chip thermometry in a wide range of temperature (up to 500 K).

New type of solid state refrigerator based on superconductor – semiconductor ($n^{++}Si$) – superconductor (S-Sm-S) structure with has been developed by participants in the project [2]. The operation of the S-Sm-S refrigerator is based on the existence of the energy gap in the superconductor which affects tunneling of the quasiparticles between the superconductor and the normal electrode (semiconductor). Schottky barriers form the tunneling barriers in these devices. The energy band diagram of the structure is shown on Fig. 3. Considerable cooling of the electron system in n++Si (more than 50%) in respect to substrate temperature was achieved at 150 mK. The electron temperature as a function of the bias across the double junction device at different bath temperatures is shown in Fig. 4. The lowest electron temperatures reached are around or below 30 mK Variation of the doping level in the SOI film significantly affects the resistance of the Schottky barrier [37] and the electron-phonon coupling in the semiconductor. this feature can be used for modification of the cooler device parameters in a very wide range [55].

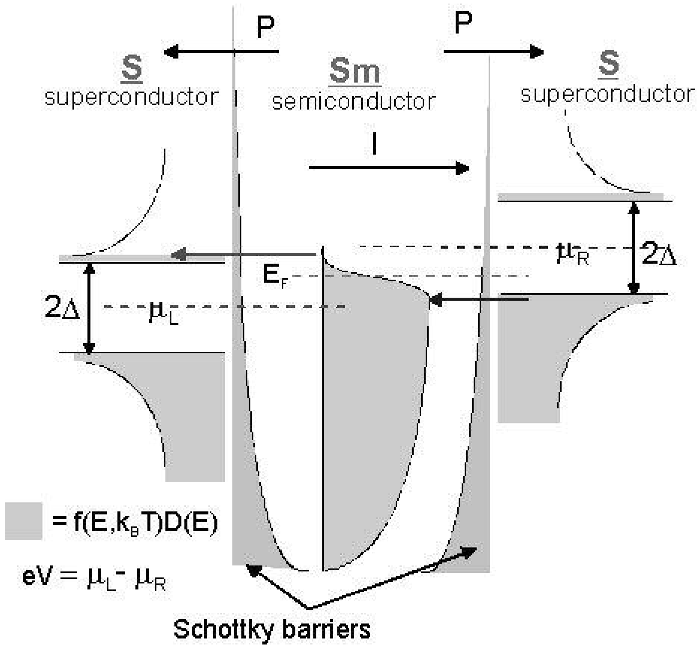

Fig. 3. Energy band diagram of an S-Sm-S microcooler. The current flows in indirection and heat is removed through both of the junctions.

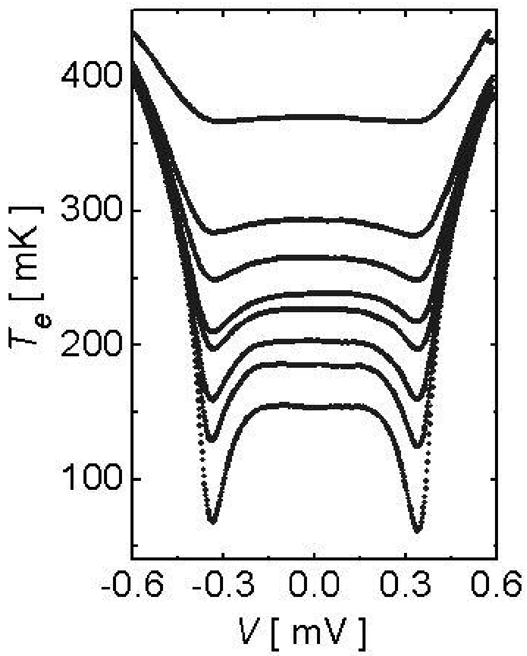

Fig. 4. Electron temperature as a function of bias voltage measured from a double junction S-Sm-S SOI cooler at different bath temperatures.

Future steps for optimisation of the S-Sm-S cooler design for higher cooling power have been suggested: modification of the cooler geometry (thickness of the Si and superconductor layers, size and shape of the SOI mesa, number and size of the S-Sm junctions), use of different superconducting materials (Al, Nb and Mo), variation of the silicon doping level, and adding additional trap layer(s) on top of the superconductor for removing hot quasiparticles and to prevent the back flow of quasiparticles into the semiconductor.

The thermal resistance between electrons and phonons (the lattice) and the thermal conductivity of the electron gas are very important issues in the applications of nanoscale structures. The coupling between electrons and phonons in heavily doped SOI film at low temperature was measured [4, 33]. The results are important both for fundamental science and for development of microcoolers. The data can be used in designing various Si based devices operating at subkelvin temperatures. The electron-phonon interaction in n-type silicon with different doping levels (electron concentration N_e = 4 - 16*10^{19} cm^{-3}) was investigated at sub Kelvin temperatures [37, 54]. The electron-phonon coupling and other parameters of the S-Sm-S structures demonstrate strong dependence on the doping level in silicon (electron-phonon coupling increases with the increase of carrier concentration). Measured electron-phonon coupling constants in heavily doped silicon are about an order of magnitude smaller than in normal metals. This makes n^{++}Si -superconductor structure a potential candidate for realization of “hot electron“ bolometers. Devices based on S-Sm structures can have better characteristics than SIN (superconductor-insulator-normal metal) structures used for this purpose previously.

The electron thermal conductivity in heavily doped silicon was investigated at sub-Kelvin temperatures [38]. In this experiment electrons were heated in a small area at the other end of a long SOI bar, and the electron temperature decay along the bar was measured. In steady state the heat flow in the system is determined by the electron thermal conductivity along the Si bar and by the energy flow rate between electrons and phonons. The behaviour of electron thermal conductivity in the SOI film is in accordance with the Wiedemann-Franz law [38].

Transport properties of InP/InGaAs heterostructures

3-5 heterostructures are very promising for high frequency micro- and nano-electronics applications and for optoelectronic devices. Two type of heterostructures were investigated: InP/InGaAs (OL and JyU).

Magnetotransport characteristics of $In_{0.25}Ga_{0.75}As$/InP heterostructures have been studied at liquid helium temperature [56]. By illuminating the sample with a red LED (characteristic photon energy 1.9 eV) we managed to increase 2D carrier concentration up to twice the value of carrier concentration in dark. The mobility increased from $1.2\cdot10^5$ cm^2/Vs to $2.7\cdot10^5 cm^2$/Vs while the 2D electron concentration increased from $3.0\cdot10^{15}m^{-2}$ to $5.8\cdot10^{15}m^{-2}$. The role of different scattering mechanisms limiting the 2D electron mobility at low temperatures has been analysed.

The III-V compound semiconductor structures were grown on InP substrates by metalorganic vapor phase epitaxy (MOVPE). InGaAs/InP was used here due to its smaller effective mass, larger energy separation between the Γ and X valleys and smaller surface state density as compared to commonly used GaAs/AlGaAs. Novel method for passivation of GaAs-based surfaces was also studied in this project [8]. Low-temperature Hall mobility of 130000 cm^2/Vs was obtained from a highly strained modulation doped InP/$In_{0.75}Ga_{0.25}As$/InP quantum well.

Optical characterization of low-dimensional structures grown by MOVPE in OL was used in extent to study carrier-related processes in quantum dots [9,10,12]. Three groups of the consortium participated in this work.

New ways to combine silicon and GaAs based structures has been the subject of intense study during the last year. In the approach developed in this consortium by VTT and OL low-cost polysilicon-on-insulator (poly-SOI) wafer was used as a template for the growth of GaAs-based quantum structures [48,50]. InGaAs quantum wells and quantum dots grown by MOVPE were used as active regions of the structure. In spite of the polycrystalline structure the optical quality of these structures in terms of luminescence intensity appeared to be surprisingly good. Low temperature PL spectra measured from such structures are shown in Fig. 5. This development may open new possibilities to fabricate monolithic structures where waveguides are based on poly-SOI and light emitters on GaAs.

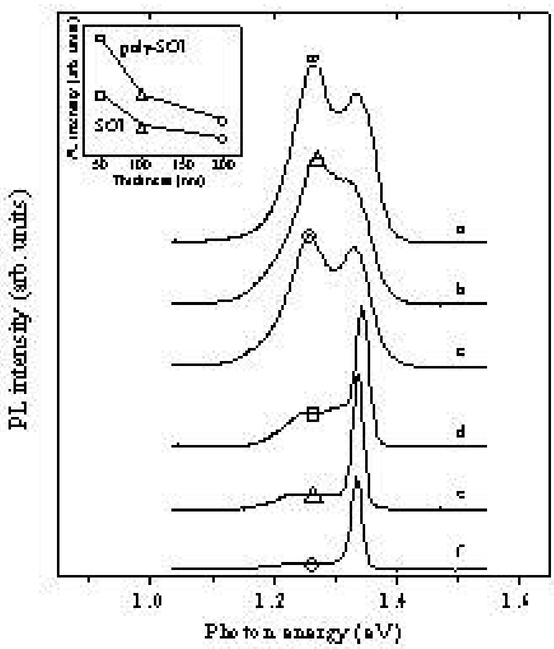

Fig. 5. Photoluminescence measured at 10 K from InGaAs quantum dots embedded in GaAs. The structure was grown on thin polysilicon film [48].

Modeling

In the modeling (LCE) of the microelectronic materials the most important achievements are theory and calculation of conductance in SOI quantum point contacts and theory and simulation of strain fields created in the SOI structures during oxidation [19,20].

It was found that the SOI quantum point contacts have a very complicated conductance pattern at low temperature regime. This was predicted by theory and confirmed by experiments. The lack of clear conductance steps (experiment) and complicated resonance pattern in the *calculated* conductance predict that the SOI quantum point contacts have randomly distributed scatterers at the Si/SiO2 interface, which is not very surprising taking into account the high density of the interface states.

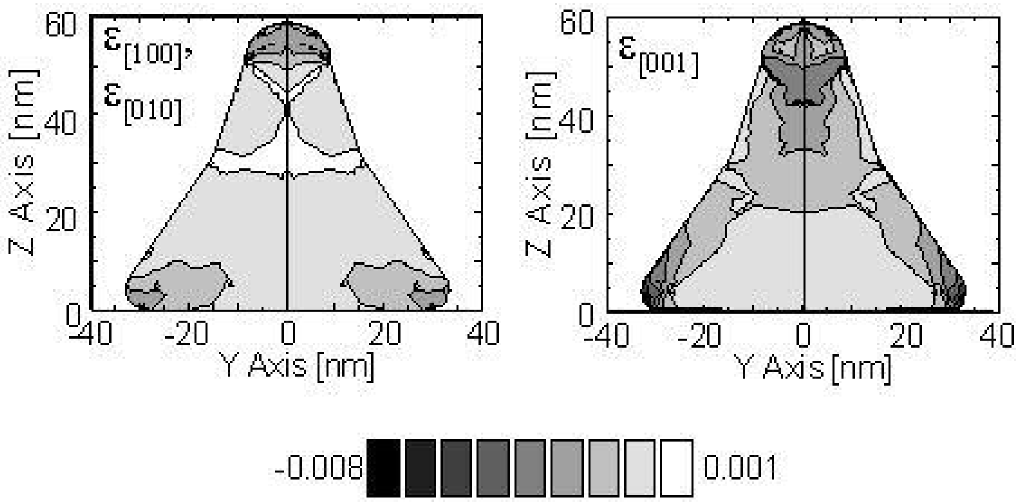

Fig. 6. Diagonal components of the strain tensor in a SOI quantum point contact. The strain distribution is given in the cross section of the conducting channel. The strain leads to deformation of the conduction band near the band minima and localization of electrons at edges of the conducting channel.

The most important outcome is information of atomic structure and strain fields as well as their influence on electronic properties of SOI quantum structures. The calculated strain distribution in a narrow SOI channel is shown in Fig. 6 We have compared results of both continuum and atomic level models and found continuum model effective down to nanometer scale structures. The modeling of oxidation, although based on simple simulation methods, has prompted us to develop a new simulation approach of complex visco elastic fluids with constitutive equation that varies as a function of space and time. The first calculations based on this new approach are in progress. Further progress is however needed in the experimental measurements to deduce the material parameters that are used in the continuum model. Note that due to large size of realistic experimental component structures, atomistic models are not computationally feasible.

2.3 Progress Report: Progress by VTT Centre for Microelectronics

In addition to the SOISETs and the Sm-S devices described above, polysilicon SETs were fabricated at VTT. The idea is that in polysilicon with the grain size of about 30-50 nm the grain boundaries form the tunneling barriers at low temperatures. Using this approach the island and the tunneling barriers do not have to be defined lithographically. Only a polysilicon bridge between the source and drain is needed. In Fig. 7 is shown a contour plot of log(I_{ds}) as a function of V_g and V_{ds} measured from such a polySiSET. The results show clear Coulomb diamonds with multiple dot characteristics, as can be expected due to the grainy nature of polysilicon.

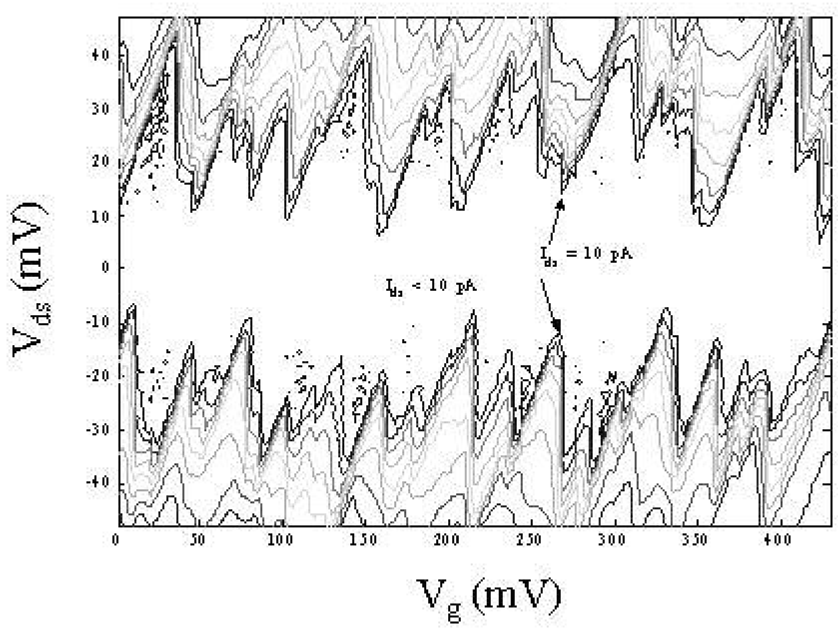

Fig. 7. Contour plot of log(Ids) vs. gate and drain-source voltages measured at 4.2 K from a polysilicon SET [M.Prunnila et al. 2001, unpublished].

2.5 Progress Report: Progress by Department of Physics, University of Jyväskylä

One of the directions which was developed in University of Jyväskylä is the investigation of the electrical and optical properties of GaAs/AlGaAs heterostructures under compression, analysis of the possibility to utilize observed phenomena for new nanodevice fabrication and for optical communication applications. The research was focused on the effect of illumination on transport characteristics of 2D electrons [56], influence of uniaxial compression on electrical and optical characteristics of the GaAs/AlGaAs heterostructures [6 ,7].

Transport properties of two-dimensional electron and hole gas at (001) GaAs/$Al_XGa_{1-X}As$ heterointerface in [110] and [1-10] directions have been investigated for the first time under in plane uniaxial compression up to 5 kbar [4]. Resistivity, Shubnikov-de Haas oscillations and Hall effect were measured and carrier densities and mobilities were determined. Without uniaxial compression the mobility is larger in the [1-10] direction in all heterostructures, this mobility anisotropy is caused by anisotropic surface roughness scattering. The in plane uniaxial compression significantly modifies the band structure of p-GaAs/$Al_XGa_{1-X}As$ that leads to strong anisotropy of hole mobility under compression. In the case of the n-type heterostructure uniaxial compression causes only change of the carrier concentration and corresponding change of the mobility anisotropy.

Theoretical calculations of intersubband light absorption spectra in p-type (001) GaAs/$Al_XGa_{1-X}As$ single heterojunctions under uniaxial compression have been performed [7]. The absorption spectrum is characterized by set of peaks at zero pressure and suffers considerable transformation under uniaxial compression. At nonzero pressure, the absorption of light with polarization perpendicular to the direction of the compression is smaller then the absorption of light with polarization parallel to the direction of the compression for the most values of photon energy.

2.4 Progress Report: Progress by the Optoelectronics Laboratory

New GaAs-based nitrides, such as GaInNAs, were developed and studied during the project [11,13,14,17]. These materials have been shown to have potential in various optoelectronic devices. High-resolution X-ray diffraction and synchrotron X-ray topography were important evaluation methods for the quality of various microelectronics materials, such as GaN, sapphire and VCz-GaAs [15,16,18].

2.6 Progress Report: Progress by the Laboratory of Computational Engineering

As a topic at LCE not listed in the research plan is the modeling of self organized quantum wires in corrugated AlGaAs /InGaAs quantum wells on vicinal (111) surfaces [22]. This material structure has strongly anisotropic conductance and optical emission. The work is underway at the University of Tokyo to grow the structure and to study conductance in a direction orthogonal to the wires in order to find Bloch oscillations in the conductance.

3 International Aspects

The large number of publications, especially in international conferences - including also invited talks, show that the dissemination of the results obtained in the project has been very active.

The collaboration between VTT and University of Tokyo (Prof. Sakaki at IIS) is very active on SOI based devices, including a preliminary accepted joint EU funded project. M. Prunnila and J. Ahopelto spent months in 2001 in Tokyo to characterize the transport properties of SOI devices, and are planning to visit IIS again in the fall 2002. VTT has been a partner in three EU projects, in which the focus of VTT has been on SOI devices. VTT has also been a partner in other two related EU funded nanotechnology projects.

J. Pekola spent a year at CRNS, Grenoble, 2001-2002, as a visiting researcher. JyU has also been carrying out research for European Space Agency (ESA) on bolometers and SINIS microcoolers.

During the MEMSS project LCE started a joint project with the Institute of Industrial Science of the University of Tokyo (Prof. H. Sakaki) on modeling self-organized quantum wires on vicinal compound semiconductor surfaces. F. Boxberg spent one month at IIS in 2000.

Low-dimensional compound semiconductors were studied in international co-operation. Juha Riikonen performed materials research on semiconductor structures using synchrotron radiation in Hasylab, Germany. International collaboration included researchers from Ireland, Germany and Poland.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, and thesis in Section 6.3.

Partner	Type of publication	1999	2000	2001	2002	**Total**	Publication numbers
VTT	Ref. journal art.	2	2	3	1	**8**	1-5,8-10
	Ref. conf. papers	4	4	9	9	**26**	23-40,42,48-50,52-55
	Monographs	-	-	-	-	**0**	
	Doctoral dissert.	-	-	-	-	**0**	
	Licentiate degrees	-	-	-	-	**0**	
	Master degrees	1	-	--	-	**1**	57
JyU	Ref. journal art.	-	1	4	2	**7**	1-7
	Ref. conf. papers	-	2	7	8	**17**	23,30-40,52-55
	Monographs	-	-	-	-	**0**	
	Doctoral dissert.	1	1	-	-	**2**	58,59
	Licentiate degrees	-	-	-	-	**0**	
	Master degrees	1	4	-	-	**5**	60-64
OL	Ref. journal art.	2	2	4	3	**11**	8-18
	Ref. conf. papers	2	1	2	6	**11**	41-50,56
	Monographs	-	-	-	-	**0**	
	Doctoral dissert.	-	-	-	-	**0**	
	Licentiate degrees	-	-	-	-	**0**	
	Master degrees	-	1	-	-	**1**	65
LCE	Ref. journal art.	1	3	1	1	**6**	9,10,19-22
	Ref. conf. papers	-	-	-	1	**1**	51
	Monographs	-	-	-	-	**0**	
	Doctoral dissert.	-	-	-	-	**0**	
	Licentiate degrees	-	-	-	-	**0**	
	Master degrees	-	1	-	1	**2**	66,67

5 Other Activities

VTT co-organized the "10th MELARI/NID Workshop" in Helsinki 1-3 July 2002. In connection with the NID meeting, a "Finnish Workshop on Nanosciences" was arranged. Prof. J. Ahopelto acted as local organizer of the meetings.

OL co-arranged a conference “4th International Conference on Materials for Microelectronics and Nanoengineering (MFMN 2002)“ 10-12 June 2002, Espoo, Finland. Professor T. Tuomi acted as the chairman of the local organizing committee.

6 Publications

6.1 Refereed Journal Articles

[1] M. Prunnila, S. Eränen, J. Ahopelto, A. Manninen, M. Kamp, M. Emmerling, A. Forchel, A., Kristensen, B. Sorensen, P. Lindelof, A. Gustafsson, Silicon quantum point contact with aluminum gate, Mat. Sci. Eng. B,**74** , 193 – 196, (2000).

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HIGH ASPECT RATIO MICROSTRUCTURES (HARMS)

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Abstract

In fabrication research deep silicon etching by ICP and electrochemical etching techniques have been explored. Main results in fabrication concern pattern and area effects in etching: loading effects, pattern size effects, pattern shape effects, nothicng. It has been shown that in addition to RIE-lag, ARDE and loading effects, ICP shows pattern shape effects, e.g. hole and trench differences for identical feature sizes. Design rules to overcome these effects have been developed, and ways of utilizing patterns effects for complex shape etching have been invented. Modeling work and phenomenology of RIE-lag and ARDE have been developed. In ECE pattern shapes have been limited by silicon crystal geometry, but we have now shown that RIE initial pits can be used to initiate complex shape macropores, such as Fresnel-lenses.

Two-dimensional photonic crystal structures have been developed. The fabrication process requires two critical steps: e-beam lithograhy and high aspect ratio silicon etching. The work has been done in collaboration with University of Joensuu who performed e-beam lithography. The process developed now is mature for the fabrication of photonic crystal applications in silicon-on-insulator (SOI). This work will be continued. Continuation project has been applied for from the Academy. Participation in European Union Frame Program 6 is being prepared.

1 Partners and Funding

Microelectronics Centre, Metrology Research Laboratory & Electron Physics Laboratory (fabrication research)

The group consists of group leader Dr. Sami Franssila, Dr. Kestas Grigoras and MSc Antti Niskanen at HUT. Intensive collaboration has been carried out with VTT Microelectronics Centre, Mr. Jyrki Kiihamäki (Electron Physics non-resident PhD student)

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HUT Optoelectronics laboratory/VTT Microelectronics Centre (photonic crystals)

The research group consists of subproject leader professor Matti Leppihalme and of postgraduate student Sanna Yliniemi. The work is done in close collaboration with the Photonics group at VTT Centre for Microelectronics.

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1999-2002. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1999	2000	2001	2002	**Total**
HUT/Opto	Academy	10	120	120	50	**300**
HUT/Metrol.	Academy	190	310	250	100	**850**
HUT El.Phys.	Academy	150	250	220	80	**700**
Total		**350**	**680**	**590**	**230**	**1850**

2 Research Work

2.1 Objectives and Work Plan

Original goals for the project were stated as:

Development of fabrication technologies for high aspect ratio microstructures, using ICP plasma etching and electrochemical macroporous silicon formation. Process integration of wafers with HARMS; especially patterning and film deposition on highly non-planar surfaces. Applications of HARMS structures in photonic crystals and microfluidic devices.

The first goal has been achieved, with results in both ICP and ECE. Process integration general approaches have been sidelined. In the applications microfluidic work has been directed towards non-lithographic ECE, in collaboration with doc. Tapio Kotiaho (now at University of Helsinki, Viikki Drug Discovery Technology Center DDTC), as presented in the proposal. Results have been obtained in mass spectrometry instrumentation (DIOS).

Nanostructures suitable for two-dimensional photonic crystal applications at the telecommunications wavelength window, around 1.55 μm, have been fabricated. The required dimensions for photonic band gap formation are: a lattice period approximately 420 nm, an air-to-dielectric filling ratio 20%-70% (corresponds a wall thickness 50-220 nm in a triangular lattice), and an etch depth around 1 μm. Silicon etching was performed by inductively coupled plasma (ICP). For impeccable optical operation, smooth, vertical sidewalls are required that puts great challenges for ICP etching.

2.2 Progress Report, fabrication

Pattern size effects, RIE-lag and ARDE and pattern density effects, loading at macro and microscale, have been studied intensively for IC fabrication in the past 10 years. MEMS structures present the same problems in extreme cases, with aspect ratios up to 40:1. In this project we have explored these effects for ICP etching, and have shown that even more delicate pattern effects do exist: pattern shapes are responsible for some etch non-uniformities.

We have shown that above 4:1 aspect ratio ARDE becomes pronounced, but for circular holes, the effect is seen for even lower aspect ratios. Profile microloading has also been studied: barreling of trenches was found to be linewidth dependent, and it limits trench spacing design rule because allowances must be made to account for barreling, which is many cases is more important than mask undercut (which is quite pronounced for the basic Bosch process).

Modeling of gas flows and etch rates in high aspect ratio cavities has been carried out [5]. Results agree nicely with experimental ICP results, even though pulsing introduces its complications into modeling.

Loading effects (area dependent etch rates) have been studied at various scales in a single wafer ICP deep etching: wafer scale, chip scale and feature scale (1-1000 μm) [12]. Etched depths were 10-500 μm, and aspect ratios up to 20:1. Pulsed ICP etching with SF_6 etch step and C_4F_8 sidewall passivation step was used with oxide masking. Very high rate >7 μm/min was found for low loading case and <2 µm/min for 100% load. Arrays and isolated lines were etched identically when chip scale pattern density was a few percent, but at 40% chip scale pattern density a 10% drop in etch rate was observed. From a test structure with variable adjacent pattern density, a reactant depletion distance of a few millimeters was determined. Loading optimization has also been tried by changing basic process parameters pressure, flow, bias power and pulse durations and ratios.

We have achieved uniform etched depth regardless of feature size by employing a combination of anisotropic plasma etching in inductively coupled plasma ICP followed by wet etching [3]. In our approach, the original feature is divided into small elementary features in a mosaic-like pattern. These individual small features are all the same size and thus exhibit identical etch rates and sidewall profiles. Final patterns are completed by wet etching: the ridges between the elementary features are removed in TMAH.

Notching effect (a.k.a. footing effect) is typical of high density plasma etching, both polygate etching in ICs as well as through wafer etching in silicon MEMS. At etching end point, rapid lateral etching due to charging effects occurs. This can be partly battled by ICP reactor design. In our approach, a metallic etch stop layer, Al, has bee utilized to eliminate notching [4].

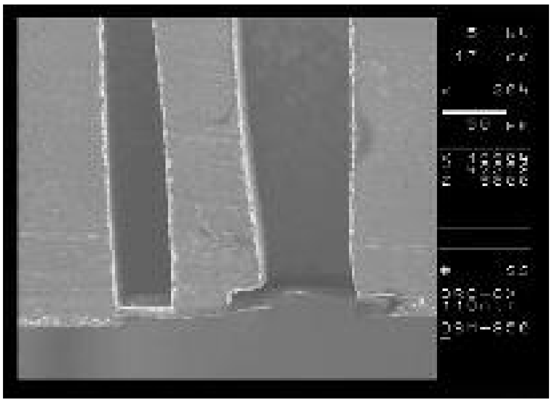

Figure 1: No notching at left, where aluminum etch stop layer has been used; wheeras oxide etch stop layer results in sever notching.

A method for producing submicron dark field patterns such as holes ortrenches is presented [2]. Using optical contact/proximity lithography with 1X masks and standard photoresist as starting points, narrow resist lines down to 200 nm have been fabricated by isotropic oxygen plasma thinning. The polarity is then reversed by liquid phase deposition of silicon dioxide from hydrofluorosilicic acid H_2SiF_6 saturated with SiO_2. This deposition takes place at temperatures below 60^{o}C, and it is selective towards photoresist. After oxide deposition, resist is stripped and reverse polarity oxide features remain. However, we have been unable to use these oxiders as ICP etching masks due to excessive film roughness and particulate deposition for thicker films that would be needed for deep etching.

Electrochemical etching ECE has been studied as an alternative to ICP. Macroporous silicon structures of different shapes were prepared by electrochemical etching of n-type silicon in diluted HF under illumination. Depths reaching 80 μm and 40:1 aspect ratios were achieved. PECVD amorphous silicon layer was used as a masking layer. Amorphous silicon was found to be quite resistant to HF etching solution. The initial pits were prepared by reactive ion etching (RIE) instead of the conventional anisotropic alkaline wet etching. Advantages of RIE made initial pits were demonstrated by electrochemically etched Fresnel lenses [1]. Electrochemically etched complex trenches with curved shapes have been demonstrated for the first time. Illumination modulation was employed to fabricate arrays of macropores with variable diameter and free standing macroporous film.

2.3 Progress Report, applications to photonic crystals

State of the art fabrication methods for high aspect ratio planar structures in silicon were developed. These structures were designed for two-dimensional photonic crystal applications. This work was performed in close collaboration with VTT Centre for Microelectronics who provided the silicon processing facilities to the use of this project. The group co-operated also with University of Joensuu and HUT Electromagnetics laboratory. Partly the same processes were utilised as in the Telectronics project "Integrated waveguide Bragg gratings" (VTT Centre for Microelectronics) funded by the Academy of Finland.

The ideas for functional photonic crystals were gathered from the knowledge obtained from wide literature published since the discovery of the photonic band gap effect at the end of 1980's. The fabrication process was then developed interactively with the finite difference time domain (FDTD) modelling results obtained from HUT Electromagnetics laboratory. The technical limitations of the fabrication put boundary conditions for the modelling which on the other hand gave more redefined information about the required dimensions in the photonic crystal structure.

Photonic band gap and the lattice structure

In order to exhibit a photonic band gap, three important things must be noticed in photonic crystal fabrication: First, materials formating the band gap must have high enough refractive index difference. Second, lattice structure must be designed so that band gap formation is possible. In two-dimensional photonic crystal applications, most promising lattice structures are triangular and quasitriangular structures. Finally, the air-to-dielectric filling ratio must be carefully chosen. High air-to-dielectric-filling ratios (over 50 %) provide larger band gap both for TE- and TM-polarisation in a triangular lattice but according to many reports [15-18] scattering losses to the third dimension grow to intolerably large values. Scattering losses to the third dimension are at the lowest when the air-to-dielectric filling ratio is approximately 20-30 %. So, a compromise between low scattering losses and a large photonic band gap must be made.

Based on the discussion above, a triangular lattice structure was chosen with cylindrical air columns in silicon background because it performs a photonic band gap at least for the TE-mode at 1550 nm [19]. Two-dimensional FDTD modelling results proposed lattice period of 420 nm and an optimal air-to-dielectric filling ratio of 56% that corresponds air hole diameter of 330 nm. The approximate value for the lattice parameter comes from diffraction theory; the lattice period must be the same order of magnitude as the wavelength in silicon at 1550 nm, that is the wavelength in vacuum divided by the refractive index of silicon. Different air-to-dielectric filling ratios were decided to be fabricated so that suitable one could be selected after the optical characterizations. According to FDTD modelling results, the etch depth in silicon should be at least one micron and the sidewall profile should be smooth and vertical. All these things put great challenges to the plasma etching method used.

Photonic crystal fabrication

Photonic crystal structures were processed on smart-cut silicon-on-insulator (SOI) wafers with an SOI layer thickness of 1 μm and a buried oxide (BOX) layer thickness of 3 μm. The fabrication procedure consisted of three critical steps to be optimized: e-beam resist patterning, oxide mask etching, and silicon etching [8]. The schematic process flow is illustrated in Fig. 1.

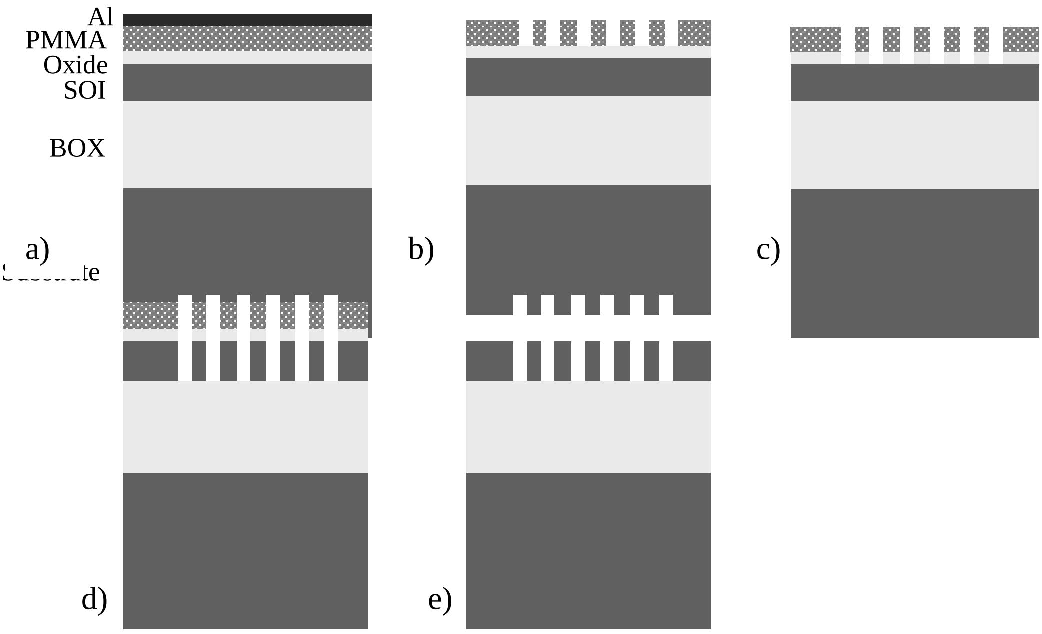

Fig. 1. A schematic picture of the process. a) Layers of the test wafer from bottom to top: Silicon substrate, 3 μm thick BOX-layer, 1 μm thick SOI-layer, 115 nm thick mask oxide, 200 nm thick PMMA-resist, and approximately 25 nm thick aluminum layer. b) Layer structure after e-beam lithography. c) The nanostructure is transferred into the mask oxide by dry etching. d) The layer structure after ICP etching. e) The final structure in silicon after resist and oxide removal.

Fabrication began with e-beam lithography to pattern a high resolution nanostructure into a polymethylmethacrylate (PMMA) resist. E-beam lithography was performed both at the University of Joensuu and at VTT Centre for Microelectronics. A thin aluminium layer on top of the PMMA resist layer was used in order to improve the conductivity of the beam electrons and, furthermore, the resolution of the e-beam lithography. After e-beam lithography the structure was transferred by dry etching into a silicon dioxide layer that was used as a hard mask in silicon etching. Oxide mask has a better selectivity in silicon etching. It also reduces the sideward pattern expansion during silicon etching. The oxide mask thickness (typically over 100 nm) was chosen so that it allowed an etch depth over one micron but did not widen the column structure too much during oxide and silicon etching.

Silicon etching was performed by reactive ion etching in inductively coupled plasma (ICP). Etching procedure with a linear passivation was used. This reduced the strong underetching in the beginning of the etching and also the sideward etching during the process and ensured smooth sidewalls. Planar dimensions were mostly controlled by the e-beam patterning although also the oxide etching expanded them significantly. The effect of silicon etching to the lateral pattern widening is negligible. The depth of the structure was determined by the silicon etch time. The notching effect described in section 2.2 was in this case avoided by reducing the platen radiofrequency bias from 13.56 MHz to 380 kHz. This enables to discharge the accumulated positive ions at the oxide interface, and no charge damage occurs.

Results

Photonic crystals with different air-to-dielectric filling ratios were fabricated. Figure 2 shows the scanning electron micrographs (SEM) of the fabricated photonic crystal structures. Filling ratios vary between 21% and 71%. The air-to-dielectric filling ratio of the photonic crystal is a result of two things: the e-beam dose and the sideward expansion during oxide etching. Since at this low dimensions exactly the same dimensions cannot be fabricated as the modelling results suggest, air-to-dielectric filling ratio must be varied around the modelling result and the optimal one has to be found in optical characterisation.

In the fabricated test structures aspect-ratios vary between 2.9-3.8 and etch detph over one micron were obtained (See Fig. 4). In two-dimensional photonic crystals these aspect ratios are well enough, and even lower aspect ratios are needed in many applications requiring single-moded light propagation. The wall verticality and smoothness are essentially important in this kind of nanostructures. From Fig. 3 can be seen that very narrow sidewalls with excellent smoothness and verticality can be fabricated. Also a strong aspect ratio dependent etching (ARDE) effect can be observed from Fig. 4. Etch depth with 200 nm diameter is only 700 nm while with larger 345 nm diameter etch depth over 1000 nm is obtained. The air column rounds the deeper the etch goes. Also this results from ARDE effect in which the etch rate slows down the deeper the etch goes when dimensions of the hole are below one micron, and also the profile is affected in deep structures by ARDE [20]. In Fig. 3 d) the etching has reached the silicon-oxide interface, and no harmful notching is observed. This indicates that lowering the platen bias frequency prevents efficiently the charge accumulation causing notching.

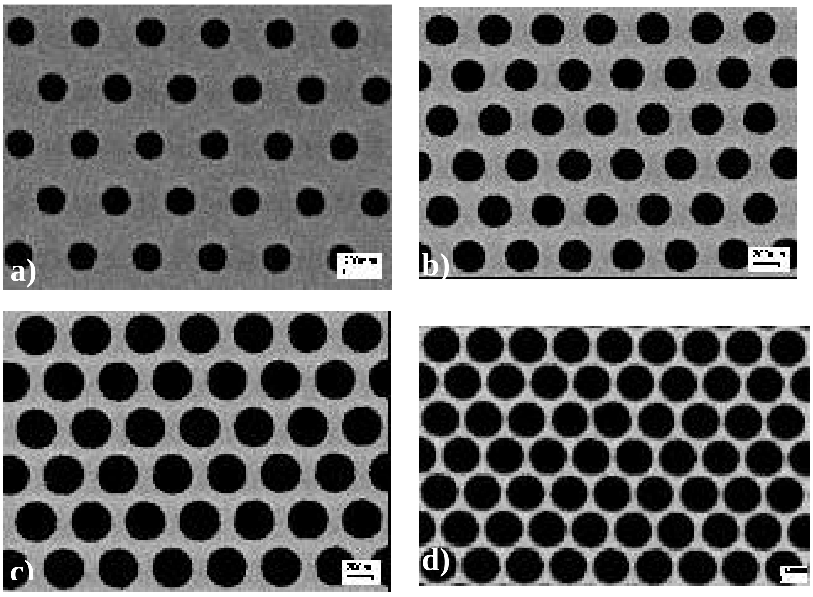

Fig. 2. SEM pictures from the top of two-dimensional photonic crystal structures after silicon etching. Diameter (d) and air-to-dielectric filling ratio (f) are a) d=200nm and f=21%, b) d=270 nm and f=38%, c) d=330 nm and f=57%, and d) d=370 nm and 71%.

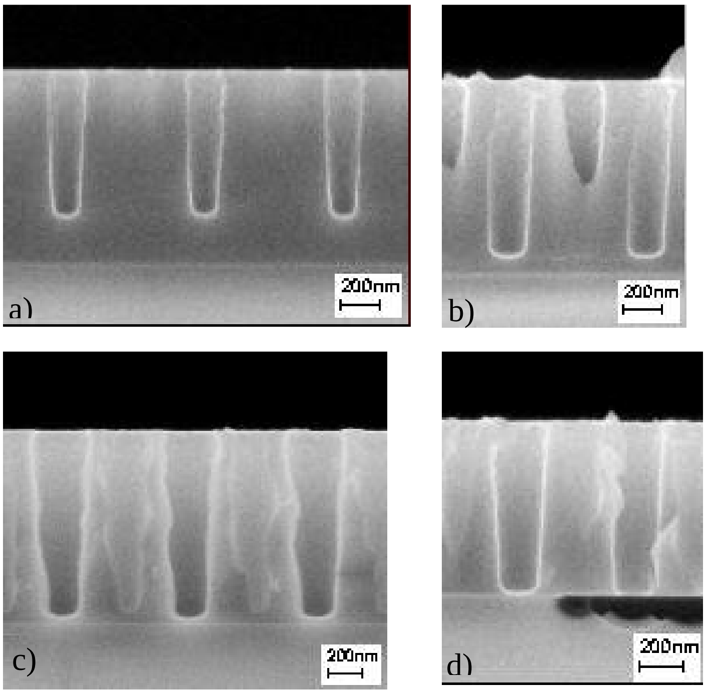

Fig. 4. Sideview profiles of the air columns after silicon etching. The etch time was 3 min with 13.56 MHz and 1 min with 380 kHz platen bias frequency. Etch depth and aspect ratio are a) 760 nm and 3.8, b) 900 nm and 3.3, c) 975 nm and 3.0, and d) 1010 nm and 2.9.

Our process is suitable for most of the planar photonic crystal applications in silicon. It is not dependent on the chosen lattice structure, also other lattice structures providing a photonic band gap and dimensions proportional to those used in this experiment can be realised with this fabrication method. Functional defects operating as waveguides, waveguide bends, Y-couplers, etc., can be created to the structure.

Three different two-dimensional photonic crystal elements in a trigonal lattice geometry were designed and modelled. These elements were waveguide bends turning light propagation direction around 60° and 120° angles and a taper element. Component dimensions for 60° and 120° angles were 7.3 µm times 6.0 µm, and for the taper element 8.4 µm times 6.3 µm. Angle elements are constructed of a straight waveguide with one missing row in ΓK-direction and a corner section where part of the air column places are changed from ideal crystal geometry in order to improve the transmission around the bend. The taper element consists of a straight photonic crystal waveguide with a tapering section that widens the photonic crystal waveguide compatible to the conventional single-moded waveguide. Taper element can be used in both input and output ends. All the elements can be integrated with each other to form more complicated components but after every corner and photonic crystal waveguide part of the power in fundamental mode is lost through scattering, material attenuation, and power coupling to higher modes. Scanning electron microscopy (SEM) pictures of all the three elements are shown later in this report (see Fig. 5).

Designed component structures were written by e-beam on SOI wafer with a high resolution. The exposure dose varied between 250 and 500 $\mu As/cm^2$. Figure 4. shows 60°, 120° angles and the taper element with 350 $\mu As/cm^2$ exposure dose after oxide and silicon etching. The air column diameter is at the center approximately 330 nm and towards the edges it reduces about 15-30 nm. The difference between diameter is caused by the proximity effect during the e-beam writing. Backscattering electrons from substrate create an additional resist exposure, and the strength of this effect depends on the feature density and symmetry. The proximity effect can be eliminated either by calibrating the dose or by reducing the diameter of the circle.

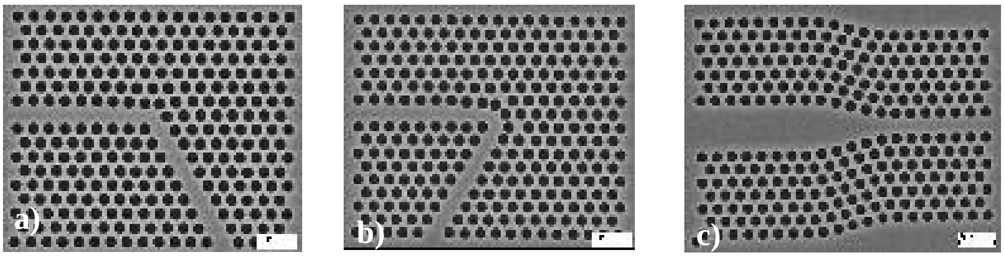

Fig. 5. Photonic crystal elements fabricated on SOI. The exposure dose was 350 μAs/cm^2. a) 60° angle element, diameter (d) is 340 nm (at edges 315), and air-to-dielectric filling factor (f) is 58% (at edges50%), b) 120° angle element, d=330 nm (at edges 320 nm), f=56% (at edges 52%), and c) taper element, d=320 nm (at edges 230 nm), f=52% (at edges 28%).

3 International Aspects

VTT Microelectronics Centre entered into an EU-project on ICP etching (SEA, Semiconductor Equipment Assesment) with Qinetics as the lead partner. Jyrki Kiihamäki ran test processing on ICP etchers at Qinetics for international evaluation of new deep reactive etching tools.

Based on the work done in this project a participation in EU Frame Programme 6 is prepared. An Expression of Interest has been sent to EU for the Network of Excellence related to photonic crystals.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project.

Partner	Type of publication	1999	2000	2001	2002	**Total**	Publication numbers
HUT	Ref. journal art.	-	3	2	1	**6**	1-6
	Ref. conf. papers	-	3	2	2	**6**	7-13
	Monographs	-	-	-	-	**-**	
	Doctoral dissert.	-	-	-	-	**-**	
	Licentiate degrees	-	-	-	-	**-**	
	Master degrees	-	-	-	1	**1**	14

5 Other Activities

Fabrication process has been developed in co-operation with HUT and VTT Centre for Microelectronics. This collaboration has included test mask design, sample processing and measurements. ICP etching has become a major technology for SOI micromechanics, with a lot of device applications at VTT. However, only those papers directly relevant to basic research in fabrication have been included in this project. Others will be included in the PhD thesis of Jyrki Kiihamäki.

Several joint meetings with HUT Electromagnetics laboratory (Prof. Keijo Nikoskinen and Tero Uusitupa), VTT Centre for Microelectronics (Päivi heimala and Timo Aalto), and HUT Optoelectronics laboratory (Prof. Matti Leppihalme and Sanna Yliniemi) has been organised. Also joint meetings with University of Joensuu, Physics department (Prof. Jari Turunen, Prof. Markku Kuittinen, Janne Simonen, and Jani Tervo), and VTT Centre for

Microelectronics (Päivi Heimala and Timo Aalto), and HUT Optoelectronics laboratory (Prof. Matti Leppihalme and Sanna Yliniemi) have been held. HUT Electromagnetics laboratory and University of Joensuu, Physics department, have performed modelling regarding photonic crystal components.

6 Publications

6.1 Refereed Journal Articles

1. K. Grigoras, A.J. Niskanen, S. Franssila: Plasma etched initial pits for electrochemically etched macroporous silicon structures, J.Micromech.Microeng. 11 (2001) 371-375

2. A.J. Niskanen & S. Franssila: Submicron image reversal by liquid phase deposition of oxide, Microelectronic Engineering 57-58 (2001) 629-632

3. J. Kiihamäki, H. Kattelus, J. Karttunen, S. Franssila: Depth and profile control in plasma etched MEMS structures, Sensors & Actuators 82 (2000) pp. 234-238

4. S. Franssila, J. Kiihamäki, J. Karttunen: Etching through silicon wafer in inductively coupled plasma, Microsystems Technologies 6 (2000) pp. 141-144

5. Jyrki Kiihamäki: Deceleration of silicon etch rate at high aspect ratios Journal of Vacuum Science and Technology A. Vacuum, Surfaces and Films. Vol. 18 (2000) Nr: 4, pp. 1385 - 1389

6. P. Heimala, T. Aalto, S. Yliniemi, J. Simonen, M. Kuittinen, J. Turunen, and M. Leppihalme, Fabrication of Bragg grating structures in silicon, to be published in Physica Scripta, 2002.

6.2 Refereed Conference Papers

7. S. Yliniemi, J. Simonen, T. Aalto, P. Heimala, Fabrication of silicon anostructures for photonic crystal applications, The 4th International Conference on Materials for Microelectronics and Nanoengineering, Espoo, Finland, 2002, 105.

8. S. Yliniemi, T. Aalto, P. Heimala, P. Pekko, K. Jefimovs, J. Simonen, T. Uusitupa, Fabrication of photonic crystal waveguide elements on SOI, presented at SPIE Photonics Fabrication Europe Conference 2002, Brugge, Belgium, 28 Oct-1 Nov, paper no.: 4944-3

9. S. Tuomikoski, K. Huikko, K. Grigoras, A.J. Niskanen, T.Kotiaho, R. Kostiainen, S. Franssila, M. Baumann: Preparation of porous n-type silicon sample plates for Desorption/Ionization Mass Spectrometry (DIOS MS), NanoTech2001, Montreux

10. K. Grigoras, T. Juvonen, K. Nera, P.Heikkilä, S. Franssila: Bulk-Micromachined Silicon Microbridges for Infrared Emitters, Abstract book of Micromechanics Europe 2001, September 16-18, 2001, Cork, Ireland

11. K. Grigoras, A.J. Niskanen, S. Franssila: Deep Silicon Structures by Electrochemical Etching, Abstract book of Micromechanics Europe (MME 2000), Uppsala, Sweden, Oct. 2000

12. A.J. Niskanen & S. Franssila: Submicron image reversal by liquid phase deposition of oxide, Abstract book of Micro and Nanoengineering (MNE2000), Jena, Germany, Sept. 2000

13. J. Karttunen, J.Kiihamäki, S. Franssila: Loading effects in deep silicon etching, SPIE Proc. Vol 4174, pp. 90-97, 2000

6.3 Monographs

6.4 Doctoral, Licentiate, and Master Theses

14. Antti J. Niskanen: Liquid phase deposition of silicon dioxide thin films, HUT, 2002 (accepted with distinction, 5/5)

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INTERFACIAL COMPATIBILITY AND RELIABILITY OF ULTRA-HIGH DENSITY SOLDERLESS ELECTRONICS

Professor Jorma K. Kivilahti[8]

Abstract

The objectives of the research were to study the degradation mechanisms by which environmental factors produce failures in high-density build-up modules and to improve the adhesion between the dissimilar materials, which are used in the preparation of solderless electronics. In the early stages of the research, the emphasis was placed on the process development and reliability characterisation as well as on theoretical survey of the environmental testing utilising corrosive gases. However, it was soon realised that the adhesion plays even more decisive role in the achievement of overall reliability of high-density build-up modules than anticipated. Thus, the research was directed more strongly to adhesion studies. The results of the research were two-fold. Firstly, the processing conditions were carefully analysed and optimised for producing high reliability integrated modules. Secondly, the adhesion improvement needed for acceptable reliability was achieved with the different processing techniques and the novel adhesion test method developed in the project. Consequently, the research effort having focus on the characterisation of new high density solderless electronics has led to significantly increased understanding of the adhesion, processing of integrated modules and innovative solutions, which are now utilised by Finnish electronics industry as well as in academic research. It is to be noted that the adhesion research continues in the laboratory of Electronics Production Technology and aims to new disruptive applications utilising the knowledge obtained in the project.

1 Partners and Funding

1.1 Laboratory of Electronics Production Technology (EPT), Helsinki University of Technology (HUT)

The research group consisted of the project leader, professor Jorma Kivilahti, post-graduate students M.Sc. Ge Jun, M.Sc. Markus Turunen and M.Sc. Ratan Saha and M.Sc. thesis students Risto Tuominen, Pirkitta Koponen, Jussi

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Särkkä, Mikko Vuorela, Tuomas Waris, Marisanna Koponen, Pia Myllymäki and Andrei Olykainen.

1.2 Funding

Funding of the project in 1000 FIM during 1999-2002. Internal funding consists of manpower costs and operational expenditures provided by Academy of Finland are shown in Table 1.

Table 1.

Partner	Funding organisation	1999	2000	2001	2002	**Total**
HUT/EPT	Academy	299	604	598	299	**1800**
Total		**299**	**604**	**598**	**299**	**1800**

2 Research Work

2.1 Objectives and Work Plan

The objectives of the research were as follows: Firstly, theoretical as well as experimental survey of the degradation mechanisms by which environmental factors produce failures at the interfaces between dissimilar materials in thin and thick film layer structures. Secondly, to design and fabricate a sensing device, which could be used to monitor the existence of detrimental substances. The third objective was to improve adhesion between dissimilar materials and to decrease the harmful effects of absorbed substances on the reliability and performance of integrated modules. Finally, the ultimate goal was set to embed active and passive components reliably into printed wiring board substrates in order to achieve fully solderless interconnection schemes.

The major observation during the early stages of the research was the decisive role of adhesion on the reliability and performance of integrated module boards (IMB) being fabricated with the fully additive build-up process developed in the EPT laboratory. Hence, the course of the research was directed to obtain a better understanding of the factors affecting adhesion between polymer and metal layers as well as providing corrective measures to improve it. Even though successful solutions to the adhesion problem were discovered, the inherent difficulties that were found out in the processing hindered the successful fabrication of the sensing device. Consequently, significant theoretical and experimental work has been carried out to solve these challenges in the fabrication of reliable of IMB structures.

2.2 Progress Report

To meet the requirements of rapidly developing electronics manufacturing, especially in portable electronics, a novel IMB technology has been developed in the EPT laboratory in the projects supported by Academia of Finland, National Technology Agency (TEKES) and the Finnish electronics industry. This technology aims to fabricating integrated electronic modules by interconnecting embedded active (ICs) and passive components into multilayer polymer substrates of very high interconnection density. This solderless technology is based primarily on photodefinable epoies and fully additive electroless plating process. Electrical Cu|Cu connections between embedded components are produced concurrently with the chemical deposition of copper conductors into the photodefined areas. Likewise, resistors, inductors and capacitors are fabricated (or embedded) and interconnected into the multilayer high density modules.

However, in order to fully utilize the possibilities of the IMB technology, one needs Cu metallised IC's to get rid of the complicated under bump metallurgy (UBM) structures as needed currently with Al metallisation. The Cu metallised IC's enable the fabrication of Cu/Cu contacts throughout the whole functional module. This is very beneficial both from the electrical and the reliability point of view, and it will simplify the fabrication process considerably [4].

Miniaturisation capability of highly integrated electronics at the printed wiring board level has been shown together with the development efforts carried out in the laboratory´s TEKES project “Fabrication of Application Specific Integrated Module Boards”.in the ETX program. The ultimate goal to fabricate reliably multilayer electronic modules without using soldering techniques was met very well – as evidenced also by the best project award among the national ETX program´s 194 projects. Figure 1 shows the level of integration that was achieved and electrically characterised [10,12,13,23-28]. It was demonstrated that not only passive component like resistors, capacitors and inductors but also active components were successfully embedded and interconnected inside the functional modules.

However, the yield of the fabrication process was not satisfactory in the beginning and the reliability problems – being anticipated to relate to inadequate adhesion in the fabrication stage - arose in the environmental testing. Therefore, the materials and process development was initiated and the co-operation with material suppliers was engaged. Subsequent environmental testing and reliability characterisation of the integrated module boards (IMB) revealed that the adhesion plays a decisive role in the achievement of good reliability [11,22,26]. As a consequence, the research activities were directed more to adhesion studies including theoretical and experimental investigations aiming to modify and characterise the surfaces and interfaces as well as to test carefully the adhesion. However, there existed no sound method to characterise the adhesion between photodefinable epoxies and electrolessly deposited copper [29]. Methods like peel-strength test etc. give comparable adhesion values between similar test series but no explicit value per unit area is obtainable. Hence, the novel adhesion test method was developed in this project [1].

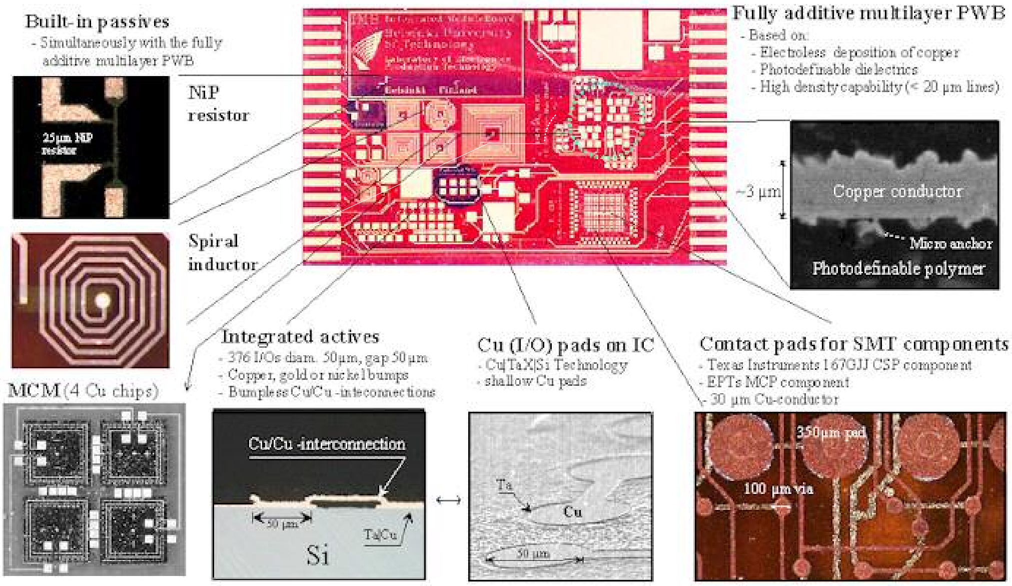

Fig. 1. Integrated module board (IMB) showing a multitude of interfaces between polymers and metals.

To explain the improved adhesion results achieved with plasma processing as well as with chemical and physical deposition techniques, more detailed surface characterisation was performed. Such methods as atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and contact angle measurements allowed the description of the existing adhesion mechanism (mechanical retention, chemical interaction etc.) [2]. However, as the work progressed, it became obvious that profound understanding of surface phenomena is extremely important in the adhesion control as well as in the fabrication process control. Several research groups have been striving for understanding the surface phenomena for a long time. Yet, there is no explicit way to characterise the surface free energy of a solid, which dictates wettability, adhesion and the formation of adsorption layers.

Direct measurement of a surface tension of a solid is impossible. However, many authors have claimed that models having experimental or theoretical background could combine the information gained from contact angle measurements to give the solid surface free energy. These models have in fact attained great attention and they are very frequently used to evaluate solid surface free energy of low-energy surfaces like polymers, wood and bioengineered tissue materials [30].

The research group examined thoroughly the theoretical justification of the most frequently used models and found out some contradictions between the experimental results and the assumptions of the models not to mention that the theory of thermodynamics was partially incorrectly applied in the models. As a result, it is our opinion that the contact angle measurements can be used to monitor wettability but the evaluated surface free energy values of solids should be taken only as indicative properties of the particular solid surface in question with known history [3]. It cannot be assumed to be a "material constant", since it depends crucially on the history of the samples, surface reconstruction etc. although many authors misleadingly claim otherwise. However, the consistence between chemical characterisation (XPS) of the surfaces and contact angle measurements (i.e. wettability development as a function of chemical modification of the surface) and adhesion strengths encourages using these methods in the follow up of adhesion properties also in future [5-9]. Especially, in such cases, where direct adhesion testing is not possible by those methods which are based on the use of mechanical force, the employment of other methods that can be used to characterise interactions between materials, like contact angle measurements, are favourable if the deficiences of the methods are clearly recognised.

As mentioned above, the IMB fabrication process was not well controlled in the early stage of the project. However, during the project several master’s theses were completed in the laboratory on the subject and most of the difficulties affecting the adhesion between polymers and metallizations (esp. Cu and Ni) were solved [23-26,28]. As a consequence, several functional modules could be now fabricated with the laboratory´s lithographic process. As an example of these are the rigid and flexible memory modules (together with Nokia, Elcoteq and Picopak) fabricated with the IMB technology. It should be mentioned that the research work carried out in the project gave strong impetus to further development of the IMB technology, which is now being implemented into production by the Imbera Electronics (established in 2002 by the Aspocomp Group and Elcoteq Networks).

It is in our current interest to expand the research work carried in this project to life-science. Biosensors have been under very extensive investigations recently, and many parameters of biomedical interest can be monitored already. However, the interaction between tissues and foreign bodies (sensing modules) is not well understood and the biocompatibility and reliability of in-vivo operating devices is not adequate. Therefore, the future research activities in the EPT laboratory involve studies on the interactions at the tissue/foreign body interface. Interfacial research results and improved understanding of interfacial phenomena that were gained during the EMMA-project can regarded as very useful for the forthcoming research activities.

3 International Aspects

The research results have been published in international journals and conferences [1-3,9,10-15]. The undersigned has giving also several invited papers in international conferences and research seminars [16-19]. There has been active cooperation with the international research partners, in particular with Tokyo University (prof. Tadatomo Suga) and Chalmers University of Technology (prof. Johan Liu), in the form of researcher exchange, concerning mainly the investigation of the adhesion between polymers and conductor metals [16,18,19]. Furthermore, there have been numerous important discussions with other international members of the project, notably with the professor C.P.Wong and James Morris from the Georgia Tech (Atlanta) and the Portland State University, respectively. The partners of the research group have contributed significantly and mutually also on gaining international visibility to the research results as well as on increasing information more widely on the research subject. Broad participation of the partners to the 4th International Conference on Adhesive Joining & Coating Technology in Electronics Manufacturing organized by the EPT laboratory turned out to be a successful forum to get to know the key persons in the area and to share research results. Student exchange has been exercised and international specialists have been invited to give short courses on related matters as well as invited lectures have been given in the partner universities. The adhesion research executed in this project had an important role also in the EU projects: Flex-Si and Adhesives in Electronics, in which the EPT laboratory has been a research member for several years.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles is given in Section 6.1, refereed conference papers in Section 6.2, other papers in Section 6.3, and theses in Section 6.4.

Partner	Type of publication	1999	2000	2001	2002	**Total**	Publication numbers
EPT	Ref. journal art.	-	-	1	8	**9**	1-9
	Ref. conf. papers	-	3	1	2	**6**	10-15
	Other papers	-	1	2	1	**4**	16-19
	Doctoral dissert.	-	-	-	1	**1**	20
	Master degrees	-	2	2	3	**7**	22-28

5 Other Activities

During the project the Finnish electronics industry (esp. Nokia, Elcoteq and Aspocomp) showed special interest towards the adhesion studies, since there is increasing need for better understanding of adhesion-related phenomena in advanced electronics production. The major results obtained are now being employed also by the Imbera Electronics (a joint venture) who is comercializing the IMB technology. Many other international companies have adapted the results and the basic ideas concerning the technology in their R&D projects. Research of the integrated module devices continues in the laboratory with the emphasis on concurrent design and modelling (electrical, thermal and mechanical) of IMB electronics in another project within the Teletronics II research program funded by Academy of Finland. During the 18-21 June 2000 “Adhesives in Electronics 2000” i.e. the 4th International Conference on Adhesive Joining & Coating Technology in Electronics Manufacturing was arranged at Helsinki University of Technology that gathered the key players of the industry and institutional research centres as well as universities world-wide. The Graduate School of Electronics Manufacturing was established in the beginning of 1998 to reinforce teaching and research activities in electronics and optoelectronics manufacturing and thereby to promote the competitiveness of the Finnish electronics industry. In addition to the research on fundamental issues in materials and manufacturing in electronics and optronics several distinguished scientists have delivered their lectures on the advanced research methods and adhesion-related subjects important in this project. Many joint meetings of the research partners were held and perhaps the most visible internationally were those arranged within the EU-project “Thematic Network – Adhesives in Electronics”.

The dissemination of the results was carried out through international publications and presentations. Likewise, the major results were disseminated domestic and international electronics companies such as Nokia, Philips, Motorola and Matsushita as well as the partner universities (Tokyo University, Georgia Tech, New York State University, Chalmers University) and the institutions (Fraunhofer ISIT, VTT Microelectronics) who expressed their great interest on the results and encouraged the exchange of information. Further, international information bureaus have spread technical information on the IMB technology. Finally, popularisation of the results was carried out in the form of generalised articles e.g. in Prosessori, which has considerable readership among in Finland.

6 Publications

6.1 Refereed Journal Articles

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[15] T. Waris, R. Saha, and J. K. Kivilahti, Manufacturing of Flexible Integrated Module Boards, The IMAPS Nordic Conference 2002, Stockholm, Sweden, 29 September - 2 October 2002, Sweden.

6.3 Invited papers

[16] J.K.Kivilahti, "Concurrent Modelling and Fabrication of High Density Functional Modules", The 10th Anniversary Celebration of the Institute of Electronics Technologies at Technical University of Dresden, the 6th of October 2000, Germany.

[17] J.K.Kivilahti, "Panel-size Manufacturing of IMB Modules", International "Microsystem Integration and Packaging" Symposium, Tokyo University, 8 June 2001, Japan.

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FABRICATION OF THIN FILMS FOR ELECTRONICS BY ATOMIC LAYER EPITAXY AND ELECTRODEPOSITION

Markku Leskelä[9]

Abstract

Atomic Layer Epitaxy (ALE), also called Atomic Layer Deposition (ALD), and electrodeposition (ED) methods were studied in preparation of thin films for microelectronics. The ALE studies contained three topics: transition metal nitride films for metallizations, oxide films for gate oxides and dielectric applications in general and metal films. ED studies contained also three areas: deposition of lead chalcogenide films for IR detectors, copper indium selenide (CIS) films for solar cells and metal bus bars to improve transparent conducting oxide (TCO) films.

Several new processes were developed for transition metal nitride (TiN, TaN) films. The metal precursors were mainly chlorides but new nitrogen precursors, more reductive than ammonia, were used.: dimethylhydrazine, tert-butylamine, and allylamine. In studies of new reducing agents for Ti(IV) and Ta(V), to replace metallic Zn used earlier, it was found that trimethyl aluminium is capable to reduce the metals to +III state. The studies of gate oxides for MOSFET transitors were focused on Zr and Hf oxide. A new process based on metal halide + metal alkoxide was developed. That process allowed the growth of the gate oxide without oxidizing silicon. Also the traditional ALD oxide processes, metal halide + water, were carefully studied for gate application. In addition, some new Zr and Hf precursors were examined. In studies of metal films the focus was at first in copper but the results obtained were only modest. Later the emphasis has been in noble metals (Ru, Pt, Ir) and very good films have been grown from metalorganic precursors and air.

PbSe and PbTe films could be deposited by ED from one solution at constant potential. The growth mechanism of PbS films was more complicated and the deposition required cycling of the potential. The ED mechanisms of lead chalcogenide films were studied by means of electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry. Electrical properties of the films were characterized as photoconductors and photovoltaic diodes. For ED of CIS films a induced codeposition was developed. The ternary compound was possible to grow from one solution at constant potential but it required strong complexation of Cu with thiocyanide. The films were closely stoichiometric and had a small excess of Cu and Se. Full solar cell structures were also prepared and characterized. For improving the TCO films Cu and Ni were electrodeposited on the side of the oxide stripes. The depositions were successful but the adhesion of the films was a serious problem.

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1 Partners and Funding

1.1 Laboratory of Inorganic Chemistry, University of Helsinki

The research group was supervised by professor Markku Leskelä and docent Mikko Ritala. The ALE group consisted of PhD Kaupo Kukli and postgraduate students Titta Aaltonen (from June 2001), Petra Alen, Timo Hatanpää, Marika Juppo (until May 2002), Petri Räisänen (until June 2001). Postgraduate students Marianna Kemell and Heini Saloniemi (until May 2000) and student Mikko Heikkilä have worked in the ED group.

1.2 Funding

Table 1. Funding of the project in 1000 Euros in 1999-2002.

Partner	Funding organisation	1999	2000	2001	2002	**Total**
UH	UH	45	45	35	35	**160**
	Academy/ EMMA	39.5	98.3	93.3	54.6	**285.7**
	Academy/other projects	35	35	85	85	**240**
	Tekes	90	90	90	75	**345**
	Industry	16	16	76	60	**168**
	Graduate school	25	25	25	25	**100**
Total		**250.5**	**309.3**	**404.3**	**334.6**	**1298.7**

2 Research Work

2.1 Objectives and Work Plan

The aim of the work was study Atomic Layer Epitaxy (ALE) (also called Atomic Layer Deposition ALD) and electrodeposition (ED) methods in preparation of thin films for microelectronics. ALE is considered as one of the most promising methods to be exploited in the near future in microelectronics for various thin film materials. ED as a simple solution technique may develop to an important method for compound semiconductor films. In this project the ALE studies contained three topics: transition metal nitride (TiN, TaN) films for metallizations, oxide films for gate oxides and dielectric applications in general and metal films. ED studies contained also three areas: deposition of lead chalcogenide films for IR detectors, copper indium selenide (CIS) films for solar cells and metal bus bars to improve transparent conducting oxide (TCO) films.

2.2 Progress Report

2.2.1 ALE studies

The main problem in the earlier existing TiN ALD process has been the high deposition temperature and in TaN process the need of Zn vapour as a reducing agent. In order to be able to TiN films below 400 ^{o}C and TaN without Zn two approaches were taken in this project. Nitrogen precursors more reactive than NH_3, namely dimethylhydrazine, tert-butylamine and allylamine, were used. Each of the precursors produced TiN films with better properties than those obtained with bare ammonia [13,28,61]. Tert-butylamine was able to reduce tantalum from pentahalide to TaN [31]. Another approach was to find other reducers than Zn vapour to be used with ammonia. Trimethyl aluminium as an additional reducing agent gave good films with reasonably low resistivity. The films contained, however, some carbon and aluminium [25,26].

Water free process of a type MCl_x – $M'(OR)_y$ opened up a new chemical approach to ALD binary of mixture oxides [7, 60]. In this chemistry the metal compounds themselves serve as oxygen precursors. Since no separate oxygen precursor is needed, the process is less oxidizing for the substrate surface. This has an enormous impact on IC technology where SiO_2 has to be replaced by high-k oxides in many applications, first in MOSFETs gate oxides. Very promising results have been obtained with this new chemistry and many metal combinations have already been studied [7,14,22,32,43]. One remarkable result of this new chemistry is the incorporation silicon into the oxide films and nearly stoichiometric Zr and Hf silicates, for example, could be made.

In gate oxide studies the focus has been in ZrO_2 and HfO_2 films. The traditional ALD process, metal chloride and water, has been studied carefully from the mechanism and electrical properties point of view [33,38]. The replacement of chloride by iodide has been extensively studied but no remarkable improvements have been obtained [11,14,23,27,35,36]. The electrical properties have been tried to improve by mixing different metals (Al, Nb, Ta to Zr/Hf) as solid solutions [3,24] or by making nanolaminates (multilayer films) [20,30,39]. Promising results, equivalent oxide thickness < 2 nm compared to SiO_2, have been obtained with Hf-Al-Nb nanolaminates. New organometallic Zr and Hf precursors, like alkoxides and aminoalkoxides have been examined to avoid halide impurities in the films [15,29,34,44]. Thermal stability is the problem of these new precursors.

Cu and Mo films had earlier been deposited by ALD from metal chlorides using zinc as a reducing agent. The dissolution and outdiffusion of Zn causes problems and therefore new processes were needed. Several copper precursors and different reducing agents were examined. Although Cu could be deposited the properties of the films were only modest [48]. Later in the project the focus in metal films was shifted to noble metals. High quality films of Ru, Pt and Ir could be grown using metallocenes as precursors and, surprisingly, air to decompose the precursors to metals [37,41,62].

2.2.2 ED studies

Lead chalcogenide thin films were deposited electrochemically from aqueous solution. PbSe and PbTe films could be deposited at constant potential while PbS was deposited by cycling the potential. The ED mechanisms were examined by electrochemical quartz crystal microbalance (EQCM) combinmed with cyclic voltammetry. Both films growth and and EQCM studies showed that the ED of PbSe and PbTe occurs by the induced codeposition mechanism, where Se (or Te) is deposited first and induces the reduction of lead to form PbSe (PbTe) at more positive potential than where Pb alone would be deposited [1,4,9]. ED of PbS turned out to be complicated including several simultaneous processes [16]. All films contained water as impurity. After annealing the films showed p-type conductivity. All films showed IR activity, the best electrical results were obtained from PbSe [47].

During the project an ED process was developed for $CuInSe_2$, which is a promising material for thin film solar cells. In the process the growth solution contained all the necessary elements including thiocyanide ions for complexation of Cu. With the thiocyanato complex it was possible to shift reduction potential of Cu to more negative values which is the requirement for induced codeposition [5,18]. If the solution contains a large excess of Cu and In ions the induced codeposition guides the stoichiometry automaticly to right values and ternary films can be deposited on a wide potential range (-0.3 - -0.65 V vs. Ag/AgCl). The films contain some water, carbon, nitrogen and sulphur

(SCN) impurities. Photoactivity studies showed that etching the films in KCN solution to remove excess Cu and Se gave best results [19]. Full solar cell structures (glass/Mo/CIS/CdS/ZnO) structures were also prepared. CdS films were made by chemical bath deposition and the different conducting oxides were studied [40]. The full structures are complicated and all films and interfaces have to optimized to obtain high photo responses. So far the values measured have been modest.

3 International Aspects

Close collaboration in ALE research has been made with University of Tartu and University of Uppsala. In ED CIS research collaboration has been made with Ecole Nationale Superieure de Chimie de Paris and Hahn-Meintner-Institute Berlin. Two European Science Foundation networks, ESF-NANO (Vapor Phase Synthesis and Processing of Nanomaterials) and ESF-ALENET (Elementary Steps of Layered Growth in the fabrication of Novel Materials by Atomic Layer Epitaxy) have been participated.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project.

Partner	Type of publication	1999	2000	2001	2002	**Total**	Publication numbers
UH	Ref. journal art.	3	12	12	14	**41**	1-41
	Ref. conf. papers	-	2	-	3	**5**	42-46
	Monographs	-	-	-	-		
	Doctoral dissert.	-	1	1	1	**3**	47-49
	Licentiate degrees	-	-	-	-		
	Master degrees	2	-	2	1	**5**	50-54
	Reviews/patents	3	-	2	3	**9**	55-63

5 Other Activities

The patents and applications are listed in Publications [59-63]. The studies and results have been presented for high school students while they have visited the Laboratory and in special days organized for them and their teachers.

6 Publications

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MULTISCALE PROCESSING AND MODELLING OF SILICON WAFERS AND STRUCTURES

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Abstract

The project combines experimental and theoretical work on silicon materials and device processing, with particular emphasis on materials and structures relevant for microelectromechanical (MEMS) devices. A versatile atomistic simulation tool, based on cellular automation/Monte Carlo techniques and first-principles calculations for reaction rates, has been developed and applied for detailed studies of anisotropic wet etching of Si. Furthermore, effect of material defect on anisotropic etching of silicon has been elaborated. Free energies of native defects have been calculated from atomistic models, and the elastic/plastic properties of silicon under large deformations have been investigated. A comprehensive study of the annealing kinetics of oxygen clusters in silicon has been carried out. Epitaxial growth, plasticity and dislocation dynamics in bulk materials and heterostructures, compound semiconductors, structural properties of amorphous silicon and silica, structural properties of nanotubes and micromechanical systems have been modelled.

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1 Partners and Funding

1.1 Laboratory of Physical Metallurgy and Materials Science (MOP), Helsinki University of Technology

The research group consists of project leader Professor Veikko Lindroos, senior researcher Visiting Professor Roman Nowak, postgraduate students Eero Haimi and Rene Herrmann, undergraduate students Jami Nieminen and Antti Ihalainen. Previously, also postgraduate student Petteri Kilpinen has been working in the project.

1.2 COMP/Laboratory of Physics, Helsinki University of Technology

The research group consists of subproject leader Academy Professor Risto Nieminen, senior researcher Juhani von Boehm, post-doctoral fellows Adam Foster and Young-Joo Lee, postgraduate students Peter Råback, Miguel Gosalvez and Matti Salmi, and undergraduate students Anna Jääskeläinen, Roope Astala and Mika Nuutinen.

1.3 Computational Science and Engineering Group, Laboratory of Computational Engineering (LCE), Helsinki University of Technology

The research group consists of subproject leader Academy Professor Kimmo Kaski, senior researchers Leonel Perondi, Jarmo Hietanen, Marco Patriarca, postgraduate students Sebastian von Alfthan, Maria Huhtala, Virpi Junttila, Ville Mustonen, Laura Nurminen and Peter Szelestey, and undergraduate students Jari Mäkinen and Tommi Peussa. Apart from EMMA funding for this group has come from various related projects and from laboratory's own budget, which along with the man-power have been used to promote the common goals of these projects and computational materials research.

1.4 Funding

Table 1. Funding of the project in 1000 FIM in 1999-2002. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1999	2000	2001	2002	**Total**
MOP	HUT (visiting Prof.)			134	68	**202**
	Academy	58	204	117	421	**800**
COMP	HUT	80	200	200	-	**480**
	Academy	135	357,5	307,5	-	**800**
	Other (EU, industry foundations)	100	120	150	100	**470**
LCE	HUT	83	250	250	166	**749**
	Academy	102	285	288	125	**800**
Total		**558**	**1416,5**	**1446,5**	**880**	**4301**

2 Research Work

2.1 Objectives and Work Plan

The main goal of the project was to develop scientific base for fabrication, processing and modelling of silicon based materials and structures for microelectromechanical (MEMS) applications. The computational research included (1) modelling of etching, (2) modelling of structural and mechanical properties of silicon wafers and semiconductor interfaces including the fluid-solid coupling in MEMS and (3) modelling and optimisation of MEMS for acoustics applications. The experimental part included studies of wet chemical etching of silicon wafers. Research areas supported each other, because fabrication processes effect structural features achievable in final components.

The basic strategy in computational work was to use a multiscale approach, which means that results obtained first at the microscopic (*i.e.* atomistic) level are used to model meso-scale (*i.e.* nanometer to micrometer) and eventually also macroscale phenomena. The microscale properties necessitated the use of quantum physics methods, such as the density-functional theory widely applied in electronic-structure and total-energy calculations. Mesoscale phenomena were in turn approached via molecular-dynamics, cellular automation and kinetic Monte Carlo simulations for such processes as surface reactions, mass transport and dislocation dynamics. Finally, continuum equations were used to model macroscale phenomena, such as long-time annealing of defect-related phenomena and dissipative (gas) damping.

2.2 Progress Report: Common Themes

The three common themes of the project were:

(i) development of an atomistic model and simulation tool for anisotropic wet chemical etching of three-dimensional Si structures, used in detailed analysis of experimental etching studies;

(ii) characterisation of basic materials/electronic properties for relevant materials and structures, in particular the elastic/plastic properties of Si at large deformations and the systematic study of diffusion and long-term annealing mechanisms relevant for thermal processing of as-grown and/or as-implanted materials.

(iii) the dissipative damping of microscale silicon structures vibrating in rarefied gases.

In the following, results presented in joint publications has been covered. Other common theme results have been presented in progress reports of the laboratories.

2.2.1. Anisotropic wet chemical etching of silicon

COMP and MOP have developed an atomic-scale simulation tool for anisotropic wet chemical etching of crystalline Si [1]. This tool has been extensively used in analysing experimental results for the dependence of etch rates on crystallographic orientation, temperature, etchant concentration, and surface conditions. The model utilises the dependence of the removal probability of a given surface atom on its atomistic neighbourhood, and is realised in terms of a versatile cellular automaton. The model predicts the existence of fastest-etched planes in good agreement with experiment, described accurately the evolution of under-etching below the masks for all orientations, including the slopes of planes appearing below the mask.

The development of simulation capabilities of anisotropic wet chemical etching of silicon has industrial implications offering possibilities to reduce the present need of experimental work in manufacturing design of MEMS device.

2.3 Progress Report: Laboratory of Physical Metallurgy and Materials Science

In addition to the joint efforts, a summary of main results achieved by the Laboratory of Physical Metallurgy and Materials Science has been given here.

2.3.1 Evolution of surface roughness in anisotropic etching of silicon caused by material defects

In proper etching conditions typical (100) surface roughness of KOH etched silicon build up from shallow pits, which origin have not been unanimously explained. In the present work the effect of bulk micro defects on the surface roughness were studied using scanning infrared microscopy, etching experiments and surface roughness characterisation with Nomarsky type optical microscope. The results support the assumption that the shallow pits observed on (100) surfaces of silicon after KOH etching are caused by bulk micro defects [2].

The role of various material defects in anisotropic etching of silicon is of interest in association with precise etch rates and also surface roughness of other crystallographic planes than (100) as well. Further studies are currently in progress with project funding provided by Tekes and Finnish industry.

2.3.2 Prediction of nanoscale structure of porous silicon from processing parameters

Porous silicon has attracted considerable interest during last decade because of its quantum-confined optical properties. Furthermore, the reactivity of the large specific surface area of porous silicon is interesting as far as MEMS applications are concerned. The most common fabrication method for porous silicon is electrochemical etching in HF-based solutions. The present study concerned the dependence of porous silicon layer growth rate dh/dt on electric current density i as well as on HF concentration. The formation of a porous silicon layer was found to follow a generic linear relationship

$$\ln(dh/dt) = C + k\ln(i) \qquad (1)$$

irrespective of the processing conditions. An equation with similar form was derived from the Faraday equation, which allowed us to reach conclusions on the relationship between the growth rate dh/dt and the degree of porosity, constituting a first step in prediction of the nanoporous structure of silicon based on processing parameters. This electrochemical approach complements physical models of silicon pore formation [43].

2.3.3 Characterisation of mechanical properties of silicon with nanoindentation

Nanoindentation experiments were carried out in various silicon samples in order to characterise the properties of the materials meant for MEMS applications. The specimens were examined using ultra-micro indentation system UMIS-2000 located at Nagoya Institute of Technology in Japan, which was equipped alternatively with a triangular diamond pyramid (Berkovich type of indender) or spherical diamond tip. The applied maximum indentation load ranged from 5 to 500 mN. The indentation load-depth data were registered according to the standard instrument procedure. The performed spherical indentations accomplished in the loading-partial unloading mode allowed us to avoid effect of crystal orientation. They were found as the most suitable approach to the single crystal silicon. They proved to be useful to detect thin layers on silicon surface.

To determine elastic properties of silicon and silicon structures, we performed FEM-simulation of the penetration process to obtain proper match for the experimental data. This allowed us to conclude on mechanical properties of the examined structures. The indentation test appears to be an invaluable method for examining MEMS materials, since it requires very small volume of the solid, and probes the surface layers of particular interest. At the moment, the results has not been published yet.

2.3.4 Non-destructive experimental characterisation of bulk micro defects in silicon with scanning infrared microscopy

Elaboration of defect measuring methodology with scanning infrared microscopy is a subject of Rene Herrmann´s thesis work that is in progress.

2.4 Progress Report: COMP/Laboratory of Physics

Here we give a brief summary of the main results obtained in the project, concentrating on the applications of theoretical and computational modelling to the actual materials/structures problems. Less attention is paid to the ongoing development of new theoretical tools and computational techniques, which is an integral part of our activity as well.

Our work in computational materials science is widely recognised, both nationally and internationally. A sign of the national recognition is the status of COMP as a Centre of Excellence designated by the Academy of Finland for 2000-2005. An example of the international recognition is the large number of invited talks given by COMP members at international conferences. Related to this project, we have given more than 5 invited and plenary talks at international conferences during 1999-2002.

2.4.1. First-principles calculations of etching reactions

We have carried out extensive electronic structure calculations for the interaction of hydroxyl radicals (OH^-) and hydrogen atoms (H) with Si surfaces. These calculations, which use state-of-the-art techniques and cluster models for the surface, yield the geometries and potential-energy hypersurfaces for a large variety of structures with different atomistic environments (*e.g.* number of neighbouring Si atoms, number of preadsorbed H and OH ions *etc*.). The potential-energy hypersurfaces can then be used to construct relative reaction rates for different configurations. These in turn can be used as input in the cellular-automaton etch simulator described above. The combination of atomistic calculations and discrete stochastic simulations enables the systematic study of etching as a function of surface coverages, etchant concentrations, and temperature [3], [4].

This work has been carried out in collaboration with the HUT group in the Laboratory of Physical Metallurgy and Materials Science.

2.4.2. Calculation of defect free energies and elastic/plastic properties of silicon under large deformations

Based on a tight-binding model for silicon-silicon interactions, we have used molecular-dynamics simulation and thermodynamic integration to obtain temperature-dependent free energies for native defects (vacancies and interstitials) in silicon [5]. These in turn enable the estimation of absolute defect concentrations and self-diffusion constants. Our simulations provide a consistent interpretation of experimental self-diffusion data over a wide range of temperatures. This work constituted the M.Sc. thesis project of Ms. Anna Jääskeläinen.

The tight-binding model has also been used in a study of the nanoindentation of silicon surfaces using STM tips [6]. The molecular dynamics simulations reveal the atomistic mechanisms responsible for the irreversible work done during indentation, and provide information on the elastic/plastic response of surfaces with different orientations.

We have carried out accurate total-energy calculations for Si under large-amplitude tensile stress along different orientations. These can be used to extract information on the nonlinear elastic properties of the material, which are reflected in high-frequency mechanical oscillators based on Si. The work has been carried out in collaboration with VTT Microelectronics (Dr. Tomi Mattila), where the shape of mechanical resonance curves has been measured to a high precision. These curves can be analysed in terms of anharmonic force constants which can be compared with theoretical values [7].

2.4.3. Development of computational tools for simulating crystal-growth phenomena

During this project, we have collaborated closely with CSC Ltd. in developing finite-element-based modelling tools [8] for crystal growth of silicon materials, in particular the Czochralski growth from melt and the sublimation growth from the solid phase (in the case of SiC). The macroscopic approach used combines fluid flow simulations with kinetic rate equations for surface processes, and can utilise the microscopic results obtained in other parts of the multiscale approach.

This project continues and is carried out in collaboration with Okmetic Ltd.

2.4.4. Oxygen and boron in silicon

COMP has participated in another EMMA project (MACOMIO) by semiconductor materials modelling, focusing on compound materials and questions related to defects and doping. There is obviously a strong link to the present project on silicon materials, especially as regards the behaviour of dopants (such as B) and unwanted impurities (such as O originating from the Czochralski process). Most of the results concerning Si doping and contamination have been reported and discussed in the context of MACOMIO, and just a few main results are mentioned here.

We have studied extensively the properties of oxygen in silicon, dissolved from the quartz crucible into the material during the Czochralski growth from molten silicon. large-scale electronic structure and total-energy calculations have been carried out to obtain the properties of oxygen complexes ranging from single interstitials to chains of up to 15 oxygen atoms. The fingerprinting of these complexes has been made through calculations of both their electronic properties (donor character, metastability) and vibrational properties, experimentally accessible via Raman and IR techniques. The migration barriers for moving oxygen complexes have been calculated through detailed mapping of the potential energy hypersurfaces. Kinetic equations describing the possible migration, association, dissociation and restructuring processes of moving oxygen clusters have been solved. This enables a detailed study of the annealing kinetics of thermal double donors, which we can unambiguously associate with the various chain structures. This work solves many long-standing problems associated with thermal-donor kinetics, and has been described in detail in a number of publications (see *e.g.* [9]).

The microscopic calculations yield a large amount of data for migration barriers, dissociation and association energies, diffusivities etc. which are used in kinetic Monte Carlo simulations of aggregation and annealing phenomena. The kinetic Monte Carlo approach transcends the rate-equation methods in that it also carries information on the three-dimensional geometry of the aggregates, not only their average concentrations. The kinetic Monte Carlo work constitutes the Lic.Tech. thesis of Matti Salmi.

Boron is implanted as a dopant in silicon structures. Implantation produces defects (vacancies and interstitials) which interact with the moving boron during thermal treatment. The mechanisms responsible for the transient-enhanced diffusion (TED) processes associated with dopant implantation are still widely debated.. To elucidate the properties of boron migration in silicon, we have carried out detailed first-principles molecular dynamics simulations of its motion [10].

2.4.5. Gas damping of vibrating Si structures

We have developed a Monte Carlo simulation tool for modelling the interaction of rarefied gases with vibrating Si structures (such as those found in pressure sensors and other resonators). The approach is based on the ballistic collisions of gaseous molecules among each other and with the moving surfaces, described in terms of phenomenological cross-sections. This approach is necessary in the limit of large Knudsen numbers, where the collisional mean free paths become comparable to the dimension of the microsystem.

This work is the M.Sc. thesis project of Mika Nuutinen, and has been carried out in close collaboration with a TEKES funded project involving sevearl industrial companies. We have been able to utilise the synergy between this work and the atomistic modelling of Si structures in the other subprojects.

2.5 Progress Report: Laboratory of Computational Engineering (LCE)

Since in general the activities of the group in LCE focus on various issues of materials modelling, in particular on structural and mechanical properties, a clear distinction of progresses between various related projects has not been made. However, the research can been divided to work on (i) atomic scale modelling of epitaxial growth and thin film structures, (ii) plasticity and dislocation dynamics in bulk materials and heterostructures, (iii) modelling of compound semiconductors, (iv) modelling of structural properties of amorphous silicon and silica, (v) modelling of structural properties of carbon nanotubes, (vi) modelling of microelectromechanical systems, and (vii) development of atomic scale graphical visualisation tools and parallel computation methods. A more detailed account of the project progresses is given in what follows:

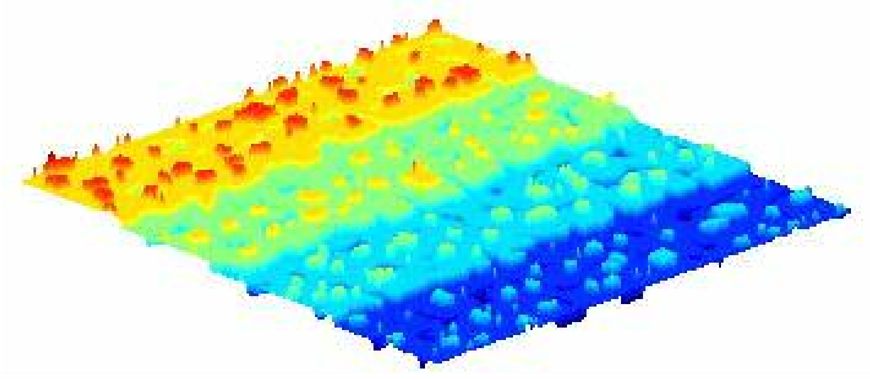
2.5.1 Atomic scale modelling of epitaxial growth and thin film structures:

Atomic level studies of epitaxial growth

Researchers: Laura Nurminen, Antti Kuronen, Kimmo Kaski

The spontaneous formation of nanoscale islands during epitaxial growth of thin films is widely recognised as a promising technique for fabricating quantum dots. We use atomic scale models in connection with kinetic Monte Carlo simulations to investigate the detailed mechanism behind the self-organisation process. Currently, we are starting a new project in collaboration with the Optoelectronics Laboratory at HUT. The purpose is to combine experimental work and computer simulations to study the initial stages in the growth of InP on GaAs.

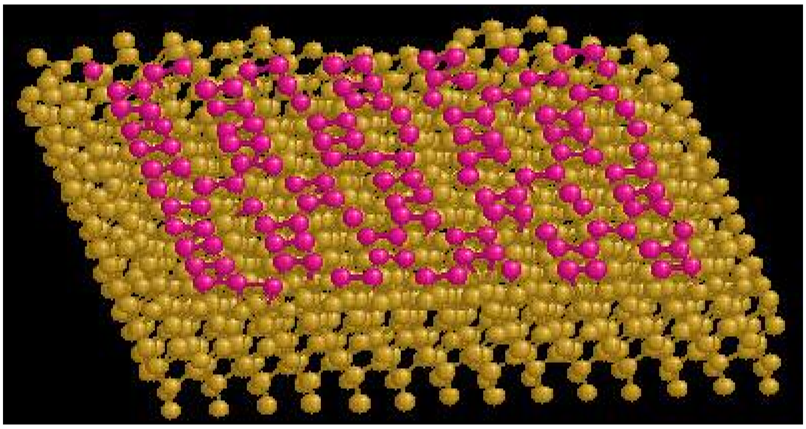
Related publications: [19] and [55]



Modelling of Thin Semiconductor Films

Researchers: Laura Nurminen, Francesca Tavazza*, David P. Landau*, Antti Kuronen, and Kimmo Kaski
*Center for Simulational Physics, The University of Georgia, Athens, GA, USA
The structure of thin semiconductor films is not only of technological importance but also offers great challenges from a theoretical point of view. The heteroepitaxial system composed of a thin layer of germanium on a silicon (001)-surface is used as an example to study the properties of mixed semiconductor systems in which lattice mismatch induced strain plays a significant role. Currently it is impossible to use ab initio methods to study systems composed of thousands of atoms. Therefore, we are using empirical interatomic potentials, such as Stillinger-Weber and Tersoff forms, to perform large-scale Monte Carlo simulations of Si or Ge layers on a Si(001) substrate.

The Si(001) surface reconstructs to form parallel rows of dimerized atom pairs. The (2 × 1) reconstruction minimises the surface energy by reducing the number of dangling bonds on the surface atoms. The empirical potentials were originally constructed with emphasis on the bulk properties of silicon. The structure of surfaces is generally much more complicated. We have therefore paid careful attention to the ability of the different empirical potentials to model the Si(001) reconstruction. Specialised Monte Carlo techniques are developed to overcome the problem of getting trapped into metastable states associated with complicated energy landscapes. Figure shows a snapshot of a simulation in which a Ge island has been deposited on a Si(001) substrate. The system is unable to reorganise into straight dimer rows, because breaking up a single dimer costs a large amount of energy. Thus the system is trapped in this metastable state.



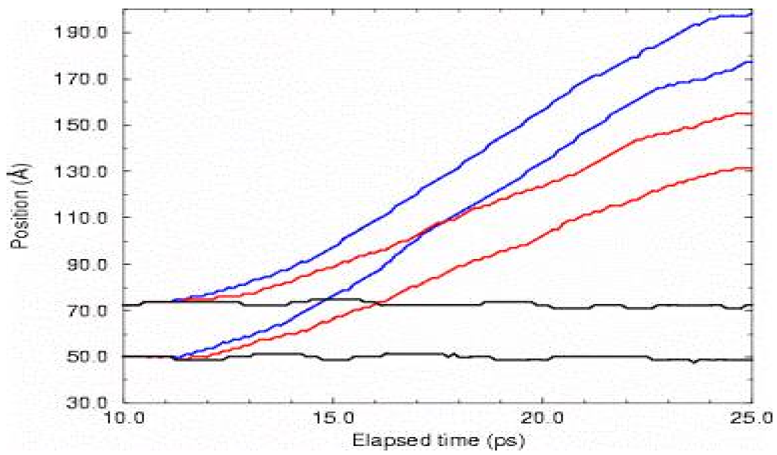
Monte Carlo simulation of a Ge island on a Si(001) surface. The Tersoff potential T3 was used to model the atomic interactions. Ge atoms are depicted in red and Si atoms in yellow.

2.5.2 Plasticity and dislocation dynamics in bulk material and heterostructures

Static and Dynamic Properties of Dislocations in FCC Metals
Researchers: Péter Szelestey, Marco Patriarca, and Kimmo Kaski

Dislocations play a fundamental role in plastic deformation of materials. Studying the structure and mobility of dislocations is important in order to understand plasticity. We studied the most common edge dislocation in FCC structures, the dissociated 1/6 a211 Schockley partial dislocations which result from the dissociation of a perfect 1/2 a110 edge dislocation. We carried out 3D atomistic Molecular Dynamics simulations using the Embedded Atom potential with the parametrization that was developed in our laboratory for four different metals (Au, Cu, Ni, Al). These potentials incorporate elastic moduli up to third-order, give reasonable stacking-fault energy, and reproduces many other material properties well. We examined the separation distance of partials, which is crucial quantity for plastic behaviour, the structure of dislocation core, and the interaction of two dislocations. We also compared our numerical results with values predicted by continuum elasticity and the Peierls-Nabarro model. Deformation of a crystal under stress is strongly dependent on the movement of dislocations. In particular dislocation velocity has direct implication on brittle and ductile behaviour. If a shear stress is applied along the gliding plane, the dislocation moves with a constant velocity which depends on the value of the shear stress and the material properties. A difficulty of this type of simulations is to make a model which represents an infinite system as well as possible. In our research we have studied the motion of Schockley partials, concentrating especially on the low shear stress regime. We have analysed the shear stress vs. velocity relation and how the separation distance changes with increasing velocity.

Related publications: [11] and [32]



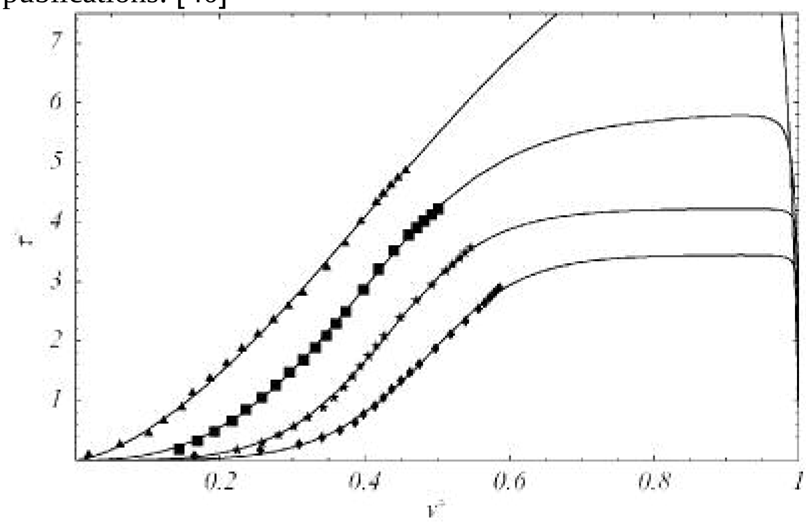
Motion of two partials under shear stress (upper and lower curves with the same colour). Black lines: no external shear, red lines: with external stress, blue lines: with larger stress.

Influence of Many-body Interactions in Stress-velocity Relation of Single Dislocation in 2D Lattice

Researchers: Miguel Robles, Ville Mustonen and Kimmo Kaski

Mechanisms of deformation of a crystal under stress are strongly dependent on the movement of dislocations. So far, the dynamics of dislocations is not well understood due to the complexity and the difficulties in modelling the phenomena. Presently, due to large improvements in computing power, large scale simulations are making it possible to study the dynamics of dislocations in a consistent way. We have been studying the influence of many body interactions in the stress-velocity relation (see Figure) of a single dislocation in a 2D lattice, using molecular dynamic software with graphical user interface previously done and reported. The physical model uses a hybrid interatomic model potential which couples Lennard-Jones(LJ) potential and the Embedded Atom Model (EAM) potential. Both parts are assembled by a parameter so that the potential can be changed to describe a pure radial interaction to a strong many body interaction in a continuous way. Setting up a constant-stress scenario, the movement of a single dislocation is tracked from zero velocity state, up to a terminal velocity state. Results have been analysed using an augmented Peierls model to seek the connection between atomic scale, continuum variables and the limiting speed of dislocations.

Related publications: [40]

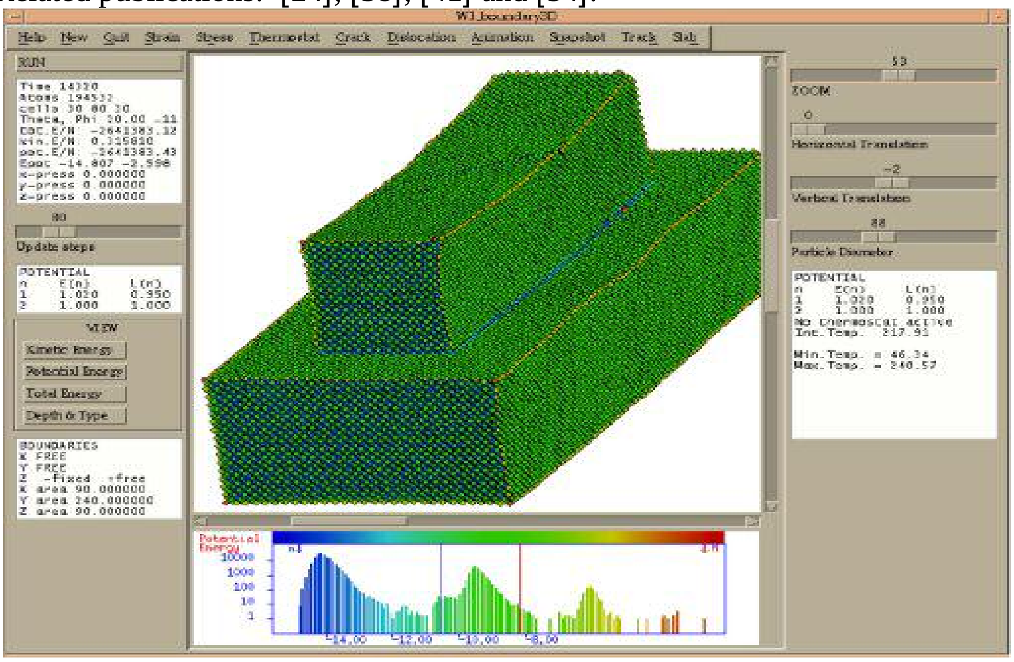


External stress-velocity relation for different values of the potential coupling parameter, upmost curve corresponds to pure LJ potential and then in curves below the many body interactions are increased. The continuum lines are result after augmented Peierls model predictions are fitted with simulation results.

Nucleation and Dynamics of Dislocations in Mismatched Heterostructures
Researchers: Marco Patriarca, Antti Kuronen, Kimmo Kaski

Dislocations, as other kinds of crystal defects, are entities with striking dynamical characteristics as well as a physical individuality, despite they are usually defined statically in terms of deviations of the lattice geometry from that of a corresponding perfect lattice. For this reason Molecular Dynamics Simulations represent a valuable tool to study their properties. We study nucleation of dislocations and dislocation dynamics in lattice-mismatched heterostructures, which have recently risen a great interest due to the technological importance of such structures. To this aim we developed a graphical user interface (Figure) from a previous 2D version, also developed at LCE, which uses a mapping based on the effective potential energy to visualise and track dislocations and other types of crystal defects. With its help we have studied the nucleation of dislocation in lattice-mismatched heterostructures for different values of the misfit and temperature. While moving, such dislocations form a stacking fault crossing the sample, whose intersection with the outer surface of the sample is clearly visible as a region of higher potential energy.

Related publications: [24], [38], [41] and [54].



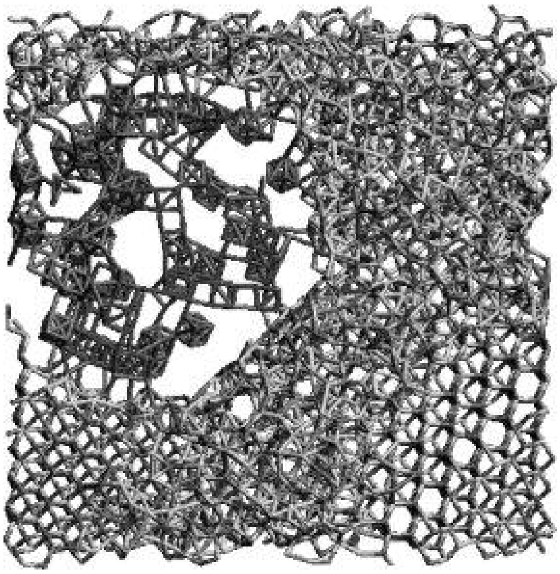
The Graphical User Interface "Boundary3D" used in the numerical simulations. In the upper graphical window a sample of the system under study is drawn, in which the colours signify the potential energy defined in the lower graphical window.

2.5.3 Modelling of compound semiconductors

Modelling of Compound Semiconductors: Analytical Bond-order Potential for Ga, As and GaAs

Researchers: Karsten Albe[*], Kai Nordlund[1], Janne Nord[1], and Antti Kuronen
[*]University of Illinois at Urbana-Champaign, IL, USA and Institut für Materialwissenschaften, TU Darmstadt, Germany , [1]University of Helsinki, Accelerator Laboratory
Various *ab initio* methods can be used to model materials at atomic level. However, due to the large demand for computational power their use is currently restricted to small systems containing up to 1000 atoms. Many phenomena like strain relaxation in heteroepitaxial systems or ion beam interaction with materials involve much larger amount of atoms. In these cases atomic level modelling has to be done using semiempirical potentials. For the III-IV compound materials there are very few potentials in the literature. We have assessed these potentials and found that their applicability for simulations in phenomena far from bulk equilibrium is poor. Therefore we have developed a new analytical bond-order potential for GaAs, that allows to model a wide range of properties of the compound structures as well as the pure phases of gallium and arsenide including non-equilibrium configurations. The analytical form follows in principle the bond-order scheme as devised by Abell and Tersoff, but angular forces and mixed interactions are treated differently. A number of tests, that cover a wide range of structural geometries including the metallic phases of gallium and arsenide, point defect properties, elastic moduli, surface properties and melting behavior, have been performed in order to validate the accuracy and transferability of the potential model.

Related publications: [25]



Structure of amorphous GaAs after melting at 1900 K at 0 pressure and subsequent cooling to 1500K predicted by the bond-order potential. Only the covalent bonds between atoms are shown. The low-density region on the upper left is a segregated As bubble which has formed during melting. On the lower left and lower right a recrystallized GaAs region has formed.

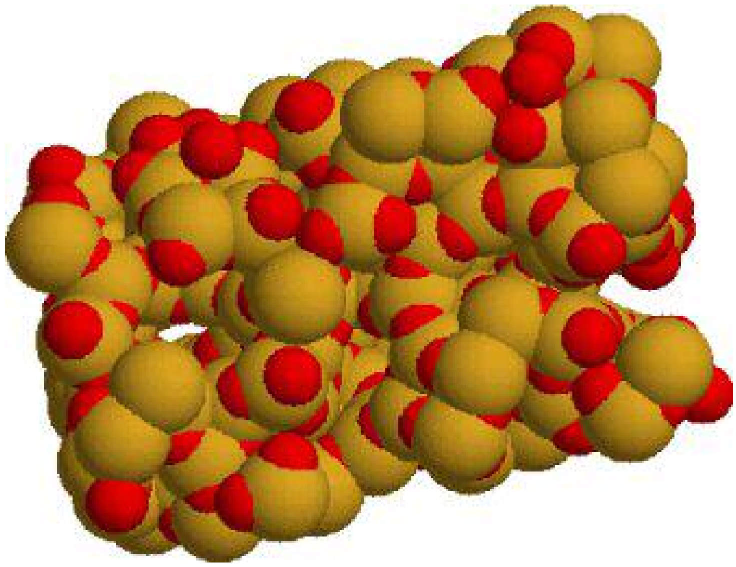
2.5.4 Modelling of structural properties of amorphous silicon and silica

Computational Study of Amorphous Silicon and Silica

Researchers: Sebastian von Alfthan, Antti Kuronen and Kimmo Kaski
Understanding of properties and structure of amorphous silica (SiO_2) and silicon is an important subject for various technological reasons. The exact structure of these materials can not be obtained experimentally but by using computational methods one can create configurations which have the same characteristics as the real ones. By studying these configurations new insight can be obtained about them. In this study models of amorphous silicon and silica have been created using two computational methods. These two methods simulate the way in which real amorphous samples are manufactured. They both start from a disordered state and by lowering the temperature of the system they reach an amorphous state. The first method is the Wooten, Winer and Weaire (WWW) method which by optimising the bond-topology of the system using a Monte Carlo scheme quenches the system to an amorphous state. Another way of creating amorphous samples is by quenching the sample from a liquid state

using a molecular-dynamics simulation, this is the 'quench-from-melt' (QFM) method. The configurations obtained are analysed using five different methods.(i) The radial distribution function is calculated and compared to experimentally obtained ones. This function shows how the distances between atoms are distributed. (ii) Distribution of angles between bonds is studied. (iii) Since amorphous silica may be porous, it is interesting to study properties of the pores. (iv) The distribution of the ring size is studied. Rings are closed paths along the bonds. (v) The vibrational density of states is studied by diagonalizing the dynamical matrix.

Related publication: [38]



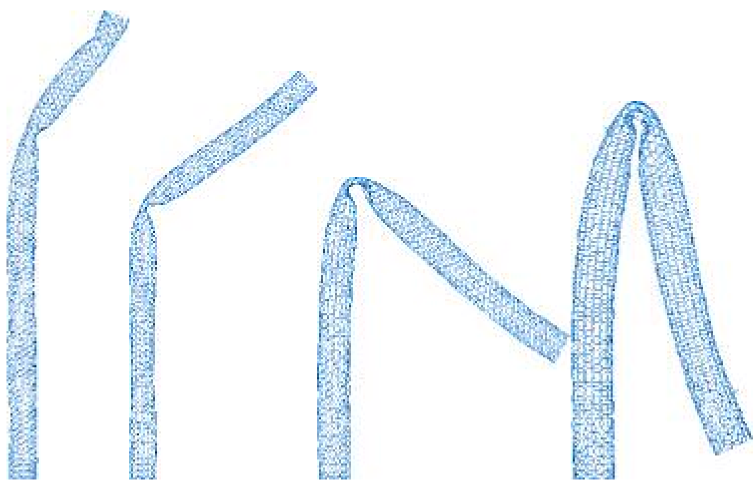
A small amorphous silica sample prepared using the WWW method.

2.5.5 Modelling the structural properties of carbon nanotubes:

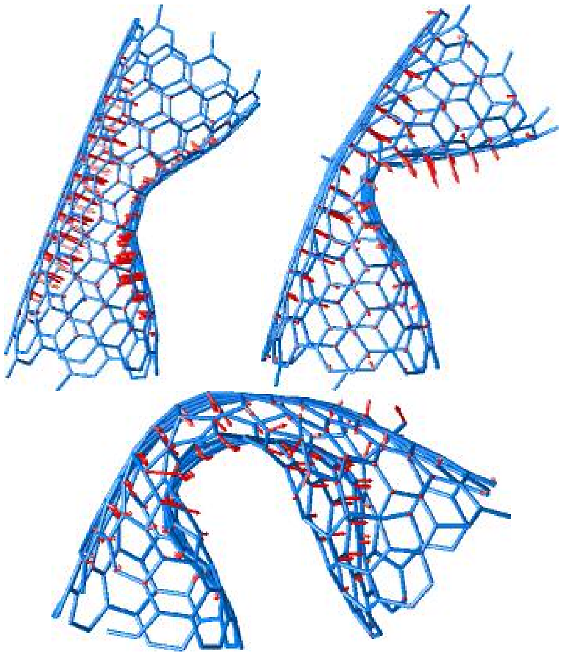
Structural Properties of Carbon Nanotubes and Nanotori

Researchers: Maria Huhtala, Kota Mogami, Antti Kuronen, and Kimmo Kaski
Carbon nanotubes are tubular all-carbon molecules with fascinating properties. Single walled nanotubes can be visualised as a graphite layer rolled seamlessly into a tubular form. Of the properties, the large aspect ratio and richness of achievable electronic properties have made carbon nanotubes the proposed material for diverse nanoelectronic and nanoelectromechanical devices whereas proposed mechanical applications rely on high elasticity combined with high yielding strength of the tubes. The properties of a carbon nanotube depend on the local atomic configuration and in many of the proposed electromechanical applications this changes from one mode of function to another. The tube can be manipulated to bend, or buckle, or defects can be induced. For device development it is essential to understand these structural changes and our work strives after shedding some more light on the occurring phenomena. The tools employed are both classical molecular dynamics and dynamical tight binding methods. Figures show a sample of a bent nanotube and more detailed images of the bend.

Related publications: [22], [23] and [37] .



A series of images depicting an (8, 8)-nanotube bending.



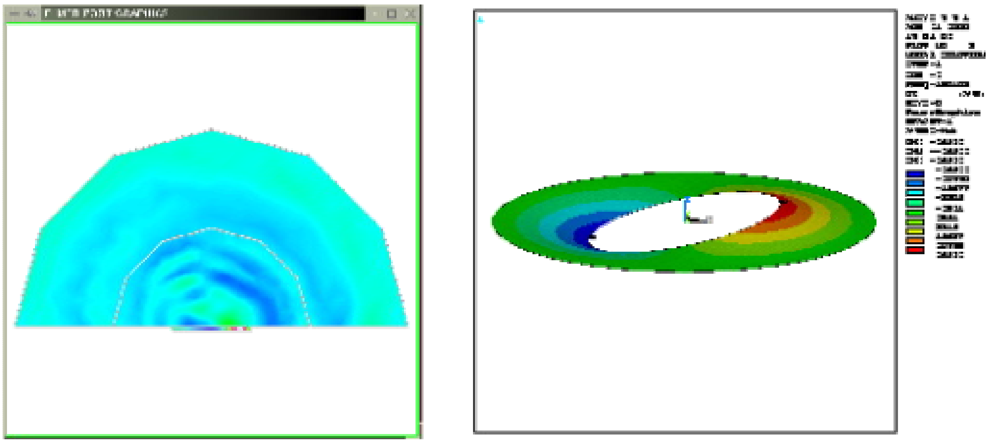
An example of observed differences between the empirical molecular dynamics model with Tersoff-Brenner interaction and the dynamical tight binding model of Frauenheim et al.. The leftmost image corresponds to the first one in the previous Figure the middle image to the next one, and the rightmost to the one after that in the previous Figure. The carbon framework is the relaxed configuration obtained by using the empirical Brenner model and the arrows indicate the displacement of atoms when relaxed with the tight binding model.

2.5.6 Modelling of microelectromechanical system:

Studies on Microelectromechanical Systems

Researchers: Virpi Junttila, Tommi Peussa, Jarmo Hietanen and Kimmo Kaski
This research is a combination of three projects: "Modelling and applications of the micromechanical systems in acoustics" and "MEMS simulations", both financed by the Academy of Finland, and "MIKSU technology program", which is partially funded by TEKES (National Technology Agency). One part of this research is MEMS related fluid-structure interaction, and its core consists of the coupling between the mechanical structure and the fluid, more specifically gas. Here attention is paid to the velocity field produced by moving structures, and to the damping of the displacement due to gas viscosity, see Figure. The modelling of these phenomena is done analytically, if possible, and using

several numerical tools, such as Ansys (ANSYS, Inc.), Femlab (Math Works), and especially Elmer, the last developed by CSC. Since in microelectromechanical systems internal flow field is related to the internal energy consumption of the device, there is a need to optimise the device structure. In non-optimised design, for instance, vortexes of fluid can be produced. If this can be avoided with more optimised design, the transducer will achieve higher performance. Also the optimal design of perforated and corrugated membranes are studied by using numerical methods (e.g. Ansys). The number and positions of holes affect the frequency range of the vibrating membrane, see Figure.



Studies of MEMS structures. On the left: Pressure field derived from Navier-Stokes equations for compressible fluid around a vibrating plate on top of a cavity (simulation done with Elmer). On the right: Displacement of a vibrating annular plate (Simulation done with Ansys).

Some related studies are made in collaboration with VTI Hamlin, Center of Scientific Computing (CSC), Nokia Research Center, Vaisala Oyj and VTT Electronics.

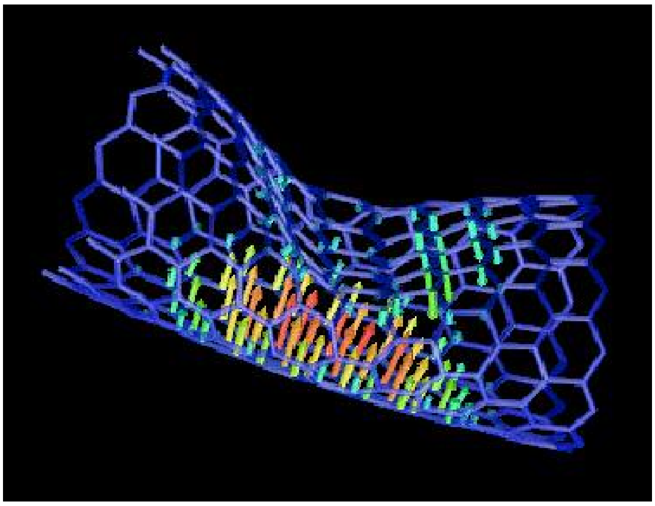
Related publications: [14], [15], [16], [17] and [18]

2.5.7 Development of atomic scale graphical visualisation tools and parallel computation method:

Online Visualisations in Computational Science

Researchers: Ville Mustonen and Kimmo Kaski
It is a well known fact that as the computers of today can be used to study increasingly complex systems, also the demands for scientific visualisations need to be considered with a proper weight. A highly versatile online visualisation environment has been built using OpenDX software package. Using this system many typical problems in computational science can be visualised online. Used approach relies on the client server type communications between simulation and visualisation. This means that simulations and visualisations can be executed with different computer systems making it possible to have online views from simulations running on parallel computers. Figure displays an example visualisation of a nanotube. The second guideline, after the main idea of having same visualisation environment for many different systems, has been low cost approach. Low cost approach means in practice, open source software (OpenDX), Linux operating system (RedHat 7.2) and fast PCs (Pentium IV) with powerful graphic cards (GeForce3). Using the above mentioned components an user friendly visualisation environment for online visualisations is established.

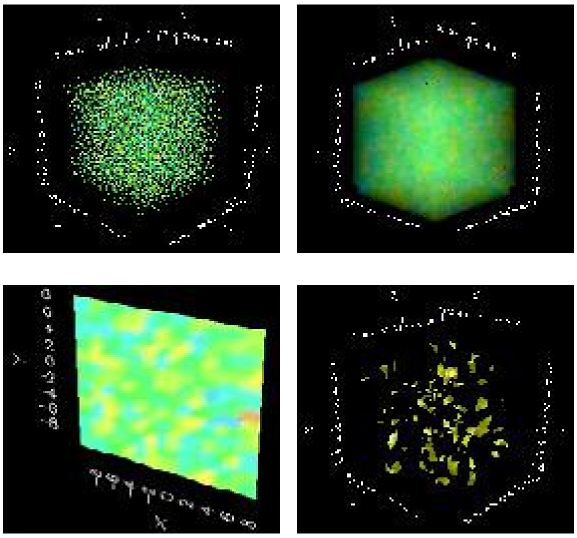
Related publication: [12]



Nanotube visualisation using OpenDX.

Large scale molecular dynamic (MD) simulations

Researchers: Ville Mustonen & Kimmo Kaski
Large scale molecular dynamic (MD) simulations are usually performed using parallel computers and algorithms in order to make the computational burden bearable. In this study a fast short-range parallel molecular dynamic simulation program is implemented and different visualisation techniques are exploited to extract defects from bulk material. Visualisation of three dimensional unstructured data is a difficult task and techniques like volume rendering and isosurfaces are used to get better insight to the studied phenomena. Online visualisation possibility is implemented to make it possible see the time evolution of the system in real time and to make the need for data storage smaller.



In most of these EMMA and EMMA-related research projects the work will continue since they represent the thesis works of the graduate students.

3 International Aspects

3.1. Long-term visitors

Prof. Roman Nowak (Hiroshima University, Japan) contributed to the project work of MOP as a visiting professor funded from other recources since 1.9.2000. He continues to work at MOP in consecutive research projects.

Mr. Rene Herrmann (Germany) is a post-graduate student at HUT, working on his thesis at MOP on the subject that is related to the project.

Dr. Young Joo Lee from KAIST, Korea has participated part-time in this project during 1998-2001 at COMP. He continues to work at COMP in related projects.

Dr. Adam Foster (University College London, UK) joined this activity as a post-doctoral research associate in 2001 at COMP. He continues to work at COMP in other related projects.

Mr. Miguel Gosalvez (Spain) is a post-graduate student at HUT, working on his thesis project at COMP. He will finish this in 2002.

Ms. Anna Jääskeläinen from COMP did part of her M.Sc. project in the group of Prof. L. Colombo (then in Milan, Italy).

Mr. Roope Astala from COMP completed his M.Sc. thesis in 1999 and moved to the group of Dr. Paul Bristowe at Cambridge University, UK. He is now moving to the U.S. as a post-doc.

Mr. Roberto Simola (University of Cagliari, Italy) did his M.Sc. thsis work on the modelling of recombination of vacancy-interstitial pairs in Si while an ERASMUS exchange student at COMP during 2001.

Laura Nurminen from LCE visited at Oxford University for 2.5 months during 2000

Maria Huhtla from LCE visited at Oxford University for 2 months during 2002

Sebastian von Alfthan from LCE visited at Oxford University for 2 months during 2002

Laura Nurminen from LCE visited at University of Georgia for 3 months during 2002.

3.2 Other international collaboration

MOP has been especially active in collaboration with Japan. Professors Tohru Sekino from Osaka University, Kazuo Sato from Nagoya University, Fusahito Yoshida from Hiroshima University, Koichi Niihara from Osaka University and

Teruaki Motooka from Kyushu University has been visiting in the laboratory in association with the project. With Professor Motooka a joint project proposal entitled "Prototype Device Formation for Wavelength Division Multiplexers and Demultiplexers by Silicon Nano-fabrication" has been prepared for Japanese and Finnish funding organizations.

COMP has hosted several short-term visitors for scientific discussions concerning this project, including Dr. Roland Madar (Grenoble), Dr. Erik Janzen (Linköping) and Dr. Rositza Yakimova (Linköping). COMP is a partner in several EU-funded European collaborations. Those relevant for this work include the □$_k$ Network, the COST P3 Activity, and STRUC Programme supported by the European Science Foundation. COMP also participates in the the Nordic network NOCDAD, supported by the NorFA foundation (post-graduate research training), on semiconductor processing and characterisation.

LCE research group on epitaxial growth has strong relations with simulation physics group of professor David Landau of University of Georgia, USA and the research group on Si and SiO2 amorphisation with professor Adrian Sutton's material science group of Oxford University, UK. Professor Landau and professor Sutton both spend several weeks in LCE every year in supervising the work of the research groups.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6

Partner	Type of publication	1999	2000	2001	2002	**Total**
MOP	Ref. journal art.	-	-	2	-	**2**
	Ref. conf. papers	-	-	-	1	**1**
	Master degrees	-	1	-	-	**1**
COMP	Ref. journal art.	1	2	2	4	**9**
	Ref. conf. papers	2	2	2	1	**7**
	Monographs	-	-	-	2	**2**
	Doctoral dissert.	1	-	-	1	**2**
	Licentiate degrees	-	-	-	1	**1**
	Master degrees	1	1	-	1	**3**
LCE	Ref. journal art.	4	6	2	2	**14**
	Ref. conf. papers	8	3	5	2	**18**
	Book chapters	-	-	1	1	**2**
	Master degrees	-	1	2	1	**4**

5 Other Activities

All three laboratories are participants of the Graduate School of Silicon Technology and Microsystems, which operates within the research area of the project. Annual seminars of the school, organized by the Graduate School Coordinator (MOP), has provided opportunities for dissemination of the project results for both domestic and international audience.

6 Publications

6.1 Refereed Journal Articles

1. M. Gosalvez, R.M. Nieminen, P. Kilpinen, E. Haimi and V. K. Lindroos: Anisotropic wet chemical etching of crystalline silicon: atomistic Monte Carlo simulations and experiments, Appl. Surf. Sci. 178, 7 (2001).
2. E. Haimi, V.K. Lindroos and R. Nowak: A First Step in Prediction of the Nanoscale Structure of Porous Silicon from Processing Parameters, J. Nanosci. Nanotech 1 (2001)2, p. 201-205.
3. M.A. Gosalvez, A.S. Foster and R.M. Nieminen: Combining Monte Carlo simulations and ab initio calculations in understanding wet chemical etching of crystalline silicon, Europhys.Lett. (in press).
4. M.A. Gosalvez, A.S. Foster and R.M. Nieminen: Atomistic simulations of surface coverage effects on anisotropic wet chemical etching of crystalline silicon, Appl. Surf. Sci. (in press).
5. A. Jääskeläinen, L. Colombo and R.M. Nieminen: Silicon self-diffusion constants by tight-binding molecular dynamics, Phys.Rev. B 64, 233203 (2001).
6. R.Astala, M. Kaukonen, R.M. Nieminen and T. Heine: Nanoindentation on silicon surfaces, Phys.Rev. B 61, 2973 (2000).
7. Y. J. Lee, R.M. Nieminen and T.Mattila, to be published.
8. P. Råback, R. Yakimova, M. Syväjärvi, R. M. Nieminen and E. Janzen: A practical model for estimating the growth rate in sublimation growth of SiC, Mat. Sci. Eng. B 61-62, 89 (1999).
9. Y.J. Lee, J. von Boehm and R.M. Nieminen: Interstitial oxygen loss and the formation of thermal double donors in Si, Appl. Phys. Lett. 79, 1453 (2001).
10. M. Hakala, M.J. Puska and R.M. Nieminen: First-principles calculation of interstitial boron in silicon, Phys.Rev. B 61, 8155 (2000).
11. P. Heino, L. Perondi, K. Kaski and E. Ristolainen. An interactive simulation program for visualizing complex phenomena in solids. In Physical Review B, 1999, Vol 60, 14625—14631.
12. J. Merimaa, L. Perondi and K. Kaski. An interactive simulation program for visualizing complex phenomena in solids . In Computer Physics Communications, 1999, Vol 124, 60—72.
13. M. Mäki-Jaskari, A. Kuronen and K. Kaski. Simulations of crack intiation in silicon. In Computational Materials Science, 1999, Vol 16, 233—240.
14. A.Rantala, S. Franssila, K. Kaski, J. Lampinen, M. Aberg and P. Kuivalainen. High-precision neuron {MOSFET} structures. In Electronics Letters, Vol 35, No. 2, 1999, 155—157.

15. J. Hietanen, J. Bomer, J. Jonsmann, W. Olthuis, P. Bergveld and K. Kaski. Damping of a vibrating beam. In Sensors and Actuators A, 2000, Vol 86, 39-44.
16. A. Torkkeli, J. Saarilahti, H. Seppä, H. Sipola, O. Rusanen and J. Hietanen. Capacitive microphone with low-stress polysilicon membrane and high-stress polysilicon backplate. In Sensors and Actuators A, 2000, Vol 85, 116-123.
17. P. Mattila, J. Stor-Pellinen, J. Ignatius, J. Hietanen and M. Luukkala. A capacitive ultrasonic transducer with a net grid backplate. In Meas. Sci. Technol, 2000, Vol 11, 1119-1125.
18. J. Hietanen and N. Zacharov. An integrated Printed Circuit Board (PCB) microphone. In Acoustical Research Letters Online, 2000, Vol 107, No 5, L25-L30.
19. L. Nurminen, A. Kuronen and K. Kaski. Kinetic Monte Carlo simulation of nucleation on patterned substrates. In Physical Review B, 2001, Vol 63, No 3, 35407-35413.
20. L. F. Perondi, K. Kaski and R. J. Elliott. Two-particle approximation to the diffusion coefficient of a tracer particle. In Journal of Physics: Condesed Matter, 2000, Vol 12, 7199-7204.
21. P. Szelestey, P. Heino, J. Kértesz and K. Kaski. Effect of anisotropy on the instability of crack propagation. In Physical Review E, 2000, Vol 61, No, 4, 3378-3383.
22. M. Huhtala, A. Kuronen and K. Kaski. Carbon nanotube structures: molecular dynamics simulations at realistic limit. In Computer Physics Communications, 2002. Accepted for publication.
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24. A. Kuronen, K. Kaski, L. Perondi and J. Rintala. Atomistic modelling of interaction between dislocations and misfit interface. In Europhysics Letters, 2001, Vol 55, No 1, 19—25.
25. K. Albe, K. Norlund, J. Nord, and A. Kuronen. Modeling of compound semiconductors: Analytical bond-order potential for Ga, As and GaAr. Physical Review B, 2002, Vol 66, 035205
26. M. Robles, L. Perondi and K. Kaski. Dynamics of Dislocation set in Motion by and External Stress. In International Journal of Modern Physics, 2001. In press.

6.2 Refereed Conference Papers

27. K. Aaltonen, J. Lehmuskoski, J. Hietanen and R. Tuokko. Precision assembly and joining of mechanical structures on printed circuit board. In S. Hahavandi and M. Saadat (Eds.) World Manufacturing congress, Proceedings of World Manufacturing Congress 1999, 493-497, Durham, UK.
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29. A.Torkkeli, J. Saarilahti, H. Seppä, H. Sipola, O. Rusanen and J. Hietanen. A capacitive microphone with polysilicon membranes. In M. Bartek (Ed). Eurosensors XIII, Proceedings of Eurosensors XIII, 13th European Conference on Solid-State Transducers, The Hague, The Netherlands, 1999, 57—60.
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Proceedings of Eurosensors XIII, 13th European Conference on Solid-State Transducers, The Hague, The Netherlands, 1999, 619—622.

31. K. Aaltonen, J. Lehmuskoski, J. Hietanen and Reijo Tuokko. Precision Assembly and Joining of Mechanical Structures on Printed Circuit Board. In S. Hahavandi and M. Saadat (Eds). World Manufacturing Congress, Proceedings of World Manufacturing Congress, Durham, UK, 1999, 493—497.
32. L. Perondi, P. Szelestey and K. Kaski. Atomic structure of a dissociated edge dislocation in copper. In Multiscale phenomena in materials - experiments and modelling. Materials Research Society Symposium Proceedings, 1999, Vol 578.
33. A. Torkkeli, J. Saarilahti, H. Seppä, H. Sipola, O. Rusanen and J. Hietanen. A capacitive microphone with polysilicon membranes. In M. Bartek (Ed). Eurosensors XIII, Proceedings of Eurosensors XIII, 13th European Conference on Solid-State Transducers, The Hague, The Netherlands, 1999, 57—60.
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37. M. Huhtala, A. Kuronen and K. Kaski. Carbon Nanotubes under Bending Strain. In Materials Research Society Symposium Proceedings, 2002, Vol 706, Z9.8..
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39. M.Patriarca, A.Kuronen and K.Kaski. Nucleation and dynamics of dislocations in mismatched heterostructures. In Proceedings of the 2001 Fall M.R.S. Meeting. 2001.
40. M. Robles, K. Kaski, V. Mustonen and M. Patriarca. The influence of many body interactions in the stress-velocity relation for one dislocation in a 2D lattice. In Proceedings of the 2001 Fall M.R.S. Meeting. 2001.
41. M.Patriarca, A.Kuronen and K.Kaski. Molecular Dynamics Simulation of Strain Relaxation in Heterostructures. In Proceedings of the XXXV Annual Conf.of the Finnish Physical Society, V.Kolhine, K.J.Eskola, V.Ruuskanen, and K.Tuominen eds., Research Report No. 5/2001, University of Jyvaskyla, Finland, 2001.
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43. E. Haimi and V.K. Lindroos, Evolution of Surface Roughness in KOH Etching of Silicon Caused by Material Defects,. 3rd Workshop on Physical Chemistry of Wet Etching of Silicon, June 4-6, 2002, Nara, Japan, p. 74-77.

6.3 Monographs

44. R.M. Nieminen: From atomistic simulation towards modelling, J. Phys. CM: Condensed Matter 14, 2859 (2002)
45. R.M. Nieminen: Multiphysics and multi-scale modelling of materials processing, Springer Lecture Notes in Compurer Science 2367, 55 (2002)

6.4 Doctoral, Licentiate, and Master Theses

46. Peter Råback: Modeling of the sublimation growth of silicon carbide crystals, Doctoral Thesis (1999)
47. Anna Jääskeläinen: Formation entropy of point defects in silicon, Master Thesis (1999)
48. Roope Astala: Nucleation of diamond in carbon onoins, Master Thesis (1999)
49. Laura Nurminen, Kinetic Monte Carlo Simulation of Epitazial Growth, Master Thesis (2000).
50. Zombor Kovacs, Characterization of Silicon with Scanning Infra-red Microscopy, Master Thesis, Technical University of Budapest/Helsinki University of Technology (2000)
51. Maria Huhtala, Molecular Dynamics Simulations of Carbon Nanotubes, Master Thesis (2001).
52. Ville Mustonen, Parallel Molecular Dynamics Simulation of Solid Materials, Master Thesis (2001).
53. Sebastian von Alfthan, Computational Study of Amorphous Silicon and Silica, Master Thesis (2002).

6.5 Chapters in books

54. Kimmo Kaski and Antti Kuronen and Miguel Robles. Computer Simulation Studies in Condensed Matter Physics XIV. Chapter:Dynamics of dislocations in a two-dimensional system. Springer Verlag. Accepted for publication.
55. Laura Nurminen and Antti Kuronen and Kimmo Kaski. Simulation of the Early Stages of Growth. In D. P. Landau and S. P. Lewis and H. B. Shuttler (Eds). Computer Simulation Studies in Condensed Matter Physics XIV. Springer-Verlag. 2001.

POROUS SILICON AS MATERIAL FOR GAS AND HUMIDITY SENSORS

Lauri Niinistö[1] and Ensio Laine[2]

Abstract

Due to its high specific area and compability with silicon technology, porous silicon (PS) is a potential material for advanced gas and humidity sensors. While the PS material itself is relatively easily prepared by electrochemical etching of silicon in hydrofluoric acid solution, the stability of PS, however, needs to be improved for use in applications. Another key to successful sensor applications is modification and control of the surface chemistry. A plausible way to control the sensitivity and selectivity parameters is by using coatings or dopants.

This investigation was focused on basic research to increase the knowledge and understanding of PS as a sensor material as well as on the effective stabilization treatments for PS and on its chemical modification for use in sensors aimed at other gases than humidity. Basic research included fabrication and structural optimization of the PS structure for sensor applications. One of the aims was to find preparative conditions which already initially produce as stable PS as possible. Research on improving the long-term stability of PS included testing of different stabilization treatments reported in the literature. Furthermore, a new stabilization method for PS, which comprises carbonization of the PS surface using acetylene as a carbon source, was developed. The new stabilisation method gives a significant improvement compared with previous methods utilizing hydrocarbon molecules. For sensor applications, PS was chemically modified by conformally coating it with potential gas sensing materials using the novel atomic layer deposition (ALD) technique. ALD processes for CuS and WO_3 were developed and CuS was successfully combined with PS and the resulting structure was tested for various sensor qualities. The ultimate goal of the project, that is demonstration of a prototype PS gas sensor, was however not yet achieved within the time frame and resources available.

Additionally, the possibilities of using birefringence for sensor applications were studied. It was, however, concluded that gas or humidity adsorption induces too small effects on birefringence for use in industrial applications. Instead, an effect in the intensity of transmitted light, which can be used to analyse the amount of water or gas condensed in a sample, was observed showing a high application potential.

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1 Partners and Funding

1.1 Laboratory of Inorganic and Analytical Chemistry, Department of Chemical Technology, Helsinki University of Technology

The research group consists of project leader professor Lauri Niinistö, postgraduate student Johanna Johansson and student Juhana Kostamo.

1.2 Laboratory of Industrial Physics, Department of Physics, University of Turku

The research group consists of subproject leader professor Ensio Laine, senior researcher Jarno Salonen, postgraduate student Mikko Björkqvist and student Jaani Paski.

1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1999-2002. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland, industry and other external sources is also shown in the table. Other external sources consisted of grants from various foundations.

Partner	Funding organisation	1999	2000	2001	2002[a]	**Total**
TU	TU	20	170	170	100	**460**
	Academy	65	335	265	200	**865**
	Industry	50	60	60	30	**200**
	Other sources	15	40	40	35	**130**
HUT	HUT[b]	10	30	30	20	**90**
	Academy	5	410	220	110	**745**
	Other sources	5	10	45	-	**60**
Total		**170**	**1055**	**830**	**495**	**2550**

[a] Includes only the period 1.1-31.7.2002
[b] Includes only direct costs excluding the salary of the project leader.

2 Research Work

2.1 Objectives and Work Plan

The main goal of the project was to demonstrate a prototype porous silicon (PS) gas or humidity sensor. To reach this goal, however, the main part of the research plan had to be focused on basic research to increase the knowledge and understanding of PS as a sensor material. This part of the research included structural optimization of PS, chemical modification of the PS surface, stabilization and adsorption optimization, and a study on the possibilities of using birefringence for sensor applications.

During the course of the project, several prototypes of PS gas sensors were reported in the international journals. Since a common problem of these prototypes was lack of stability, we refocused the priority of our objectives. Work on the structural optimization and the study of interaction of gases with the PS surface was decreased, while efforts to study the stabilization treatments and the stability itself were increased.

2.2 Progress Report: Common Themes

The overall research plan consisted of the following main steps: (i) preparation of porous silicon (PS) and understanding its material properties (ii) stabilization and modification of PS for gas sensor applications (iii) constructing a prototype PS gas sensor. Each step, especially the second one, involved extensive physical and chemical characterization where use was also made of the advanced equipment available outside the participating universities (TU and HUT), for instance the TEM facilities in Tokyo.

Because of the broad and multidisciplinary nature of the research project, the partners (TU and HUT) each focused their research on selected subtopics while the goals were jointly agreed considering the local expertise and available resources. Basically TU was developing stabilization and modification treatments while HUT was employing ALD to coat PS with gas-sensitive overlayers for final applications. There was continuous interaction between the partners through visits, project meetings and preparation of joint publications and conference presentations.

2.3 Progress Report: Progress by the Laboratory of Industrial Physics

The research at the Laboratory of Industrial Physics (LIP) started with studies of the preparative processes for porous silicon (PS). The objective of these studies was to optimise the preparative parameters of PS for sensor applications. These included the effects of the parameters on the morphology of PS (surface area, pore size distribution)[7] to already initially produce as stable PS structure against oxidation as possible [2,3].

After the optimization studies, the research was focused on the stabilization of PS. Several stabilization treatments reported in the literature were tested, and the most suitable treatments were chosen for a more detailed study in order to improve the stability of the treatments for sensor applications [e.g.,10]. Simultaneously with these studies, we adopted a method to produce SiC layer on the surface of the Si wafer to develop a novel stabilization treatment for porous silicon. The treatment is based on the use of acetylene as carbon source which decomposes and binds carbon to Si atoms when the temperature is increased [9]. Due to the small size of the acetylene molecule, almost uniform SiC coverage was obtained with this thermal carbonization treatment (TC). This was a significant improvement compared to other functionalization methods utilizing hydrocarbon molecules. In our further studies, not only a significantly improved stability against ordinary oxidation but also improved general chemical stability (KOH aq., HF) was observed in the TC treated PS [8,11,16]. More recently, the research was divided in two parts, *viz.* to study (i) high-temperature carbonization which would produce a hydrogen-free SiC surface and (ii) lower temperature carbonization which produces a hydrocarbon terminated surface (thermal hydrosilylation process). The latter surface is less stable but could offer interesting possibilities for post-treatments or for sensor applications as such.

In the initial research plan, the birefringence of PS was intended to be studied for sensor applications. However, the gas or humidity adsorption has such a small effect on the birefringence that it is not possible to use it in industrial applications. Instead, an interesting behaviour in the intensity of transmitted light was observed. Humidity, which is condensed in a pore can be desorbed with polarized laser light (HeNe, 632.8 nm) [25]. This causes variations in the transmission intensity which then can be used to quantitatively analyze how many water molecules have been condensed in a sample. Similar effect has also been observed when other vapours than humidity have been used thus indicating general validity of the method. The research will be continued in order to explore the possible industrial applications. Because of a planned patent application, the results have not yet been published.

2.4 Progress Report: Progress by the Laboratory of Inorganic and Analytical Chemistry

The research at the Laboratory of Inorganic and Analytical Chemistry (LIAC) focused, on one hand, on the modification of porous silicon in order to achieve higher gas sensitivity and, on the other hand, on testing of resulting potential gas sensor structures. The modification was achieved by conformally coating the porous material with a gas sensitive layer using ALD which can be considered a breakthrough for PS technology. This was first demonstrated by us with SnO_2 in the thesis of M. Utriainen [20]. The ALD process [17] offers several advantages for controlled growth over the conventional sol-gel coating, for instance, as demonstrated by SnO_2 [12,13,18]. Furthermore, by choosing proper coating materials both a significant gas sensitivity and stabilization of the material can be achieved at the same time.

Studies on ALD coating of PS were started with copper sulfide, a material suitable for ammonia gas sensors. The ALD process had to be optimised from the very beginning since CuS had not previously been deposited by ALD. Using optimised growth conditions smooth and conductive CuS thin films were grown on flat soda lime glass and Si(100) substrates [14]. During the project, PS was made in-house at LIAC and combined successfully with CuS. Research was continued with tungsten oxide, also a sensitive material e.g. to ammonia. Also for WO_3 an ALD process had to be developed from the very beginning. Because of weak adhesion of the tungsten precursors onto substrates during the ALD growth a successful combination of WO_3 and PS has not yet been obtained, but work needs to be continued.

The second objective was to construct a testing system for gas sensors and performing in it gas tests on different sensor materials and structures. There were several unforeseen problems and delays with the testing system and so far only tentative gas sensing results have been obtained. Studies will be continued with more a extensive gas testing research plan.

3 International Aspects

Results of the research have been presented in several international conferences. Besides the existing contacts (Hungary, Lithuania, Rumania, Netherlands), a number of new international contacts have been created during the project with groups from Italy, France, Sweden and UK. The new relations have led to fruitful further collaboration and, for example, in 2001 Dr. J. Salonen was in Kyoto University to learn to use *ab initio* calculations in FTIR studies. Now the method is used in Laboratory of Industrial Physics to connect the results obtained with FTIR and calorimetry [10]. In 2000, J. Kostamo visited the Research Institute for Technical Physics and Materials Science in Budapest to learn electrochemical etching of porous silicon and Prof. L. Niinistö gave a lecture course on thin film deposition methods focusing mainly on ALD at the Budapest University of Technology and Economics (BUTE). In addition, in 2001 J. Johansson visited Tokyo Institute of Technology to analyse modified porous silicon by TEM. Several visits have also been made to the Physics Semiconductor Institute in Vilnius in order to learn more about testing of gas sensor materials.

Parallel to the studies performed at HUT aiming at CuS thin film deposition by ALD, depositions of CuS and ternary sulfides based on CuS were also made by another chemical method, *viz*. spray pyrolysis, in collaboration with Tallin Technical University. The work has led to comprehensive reports [15,19].

A comparative study on CuS thin film deposition by gas phase chemical methods (ALD, CVD and spray pyrolysis) is also being planned. The study will be made in international collaboration where HUT is responsible for ALD, Tallinn Technical University for spray pyrolysis and probably Uppsala University for CVD. The parameters to be looked at include deposition temperature, impurities and electrical properties of the film.

As an international recognition of the work performed in the project Dr. J. Salonen was invited to be a chairman of the session “Chemical and physical sensors” in the conference “Porous Semiconductors Science and Technology” in 2002. We have also taken a part of the Nanostructured Silica- and Silicon-based functional Materials (NASSIM) Expression of Interest to the European Union 6th Framework Programme.

Another international recognition of our work is the invitation for Prof. L. Niinistö to give a plenary lecture in the forthcoming Atomic Layer Deposition

(ALD 2002) conference organized by the American Vacuum Society in Seoul, Korea in August 2002.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1999	2000	2001	2002	**Total**	Publication numbers
TU	Ref. journal art.	3	5	-	3	**11**	1-11
	Ref. conf. papers	-	-	1	-	**1**	16
	Monographs	-	-	-	-	**-**	
	Doctoral dissert.	1	-	-	-	**1**	21
	Licentiate degrees	-	-	-	-	**-**	
	Master degrees	1	-	-	1	**2**	22, 25
HUT	Ref. journal art.	-	3	1	5	**9**	7-15
	Ref. conf. papers	-	3	1	-	**4**	16-19
	Monographs	-	-	-	-	**-**	
	Doctoral dissert.	1	-	-	-	**1**	20
	Licentiate degrees	-	-	-	-	**-**	
	Master degrees	-	1	1	-	**2**	23,24

5 Other Activities

A patent application is under consideration.

6 Publications

6.1 Refereed Journal Articles

[1] M. E. Kompan, I. Yu. Shabanov, and J. Salonen, Orientation dependent Faraday effect in thin films of porous silicon, Phys. Solid State **41** (1999) 45.
[2] J. Salonen, V-P. Lehto, M. Björkqvist, and E. Laine, A role of illumination during the etching to porous silicon oxidation, Appl. Phys. Lett. **75** (1999) 826.
[3] J.Salonen, V-P. Lehto, and E. Laine, Photo-oxidation studies of porous silicon using a microcalorimetric method, J. Appl. Phys. **86** (1999) 5888.
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[5] J. Salonen, M. Björkqvist, and E. Laine, Comparison of different methods in microstructural characterization of porous silicon, J. Appl. Cryst. **33** (2000) 504.
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[10] J. Salonen, E. Laine, and L. Niinistö, Thermal analysis of hydrosilylation of 1-dodecene on porous silicon surface, Phys. Stat. Sol, in press.
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[13] C. Cobianu, C. Savaniu, P. Siciliano, S. Capone, M. Utriainen, and L. Niinistö, SnO_2 sol-gel derived thin films for integrated gas sensors, Sens. Actuators B **77** (2001) 496-502.
[14] J. Johansson, J. Kostamo, M. Karppinen, and L. Niinistö, Growth of conductive copper sulfide thin films by atomic layer deposition, J. Mater. Chem. **12** (2002) 1022-1026.
[15] P. Bombicz, I. Mutikainen, M. Krunks, T. Leskelä, L. Niinistö, and J. Madarász, Precursors for copper sulfide thin films, to be published in J. Chem. Soc. Dalton Transactions.

6.2 Refereed Conference Papers

[16] Chemical stability studies of thermally-carbonized porous silicon, J. Salonen, V-P. Lehto, M. Björkqvist, E. Laine, and L. Niinistö, Mat. Res. Soc. Symp. Proc. Vol. 638, F14.19.1 (2001)
[17] L. Niinistö, A, Volume 1, 33- 41.
[18] C. Cobianu, C. Savaniu, P. Siciliano, S. Capone, M. Utriainen, and L. Niinistö, Structural and functional dvanced thin films for electronics and optoelectronics by atomic layer epitaxy, CAS 2000 Proceedings, 23rd International Semiconductor Conference, Sinaia,

Romania, 2000 properties of SnO_2 sol-gel derived thin films for integrated gas sensors, CAS 2000 Proceedings, 23rd International Semiconductor Conference, Sinaia, Romania, 2000, Volume 2, 441-444.

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6.3 Monographs

6.4 Doctoral, Licentiate, and Master Theses

[20] M. Utriainen, Exploiting atomic layer epitaxy thin film deposition technique in solid-state chemical sensor applications. D.Techn. dissertation, Department of Chemical Technology, Helsinki University of Technology, Espoo 1999.

[21] J. Salonen, Studies on porous silicon oxidation and structure. Ph.D. dissertation, Department of Physics, University of Turku, Turku 1999.

[22] M. Björkqvist, Small-angle x-ray scattering in microstructural studies, M.Sc. thesis, Department of Physics, University of Turku, Turku 1999.

[23] J. Kostamo, Preparation of porous silicon plated with CuS for sensor applications. M.Sc.(Eng.) thesis, Department of Chemical Technology, Helsinki University of Technology, Espoo 2000.

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MATERIALS, COMPONENTS, AND MICROSYSTEMS FOR OPTOELECTRONICS (MACOMIO)

Coordinator Markus Pessa[12]
Partners Juhani Keinonen[13], Jari Likonen[14], Risto Nieminen[15], Eero Ristolainen[16], and Kimmo Saarinen[17]

Abstract

EMMA / MACOMIO focussed on five interrelated, but well-defined research areas grouped in four workparts with 93 deliverables. It was the largest basic research project on semiconductors ever carried out in Finland. It focussed on many key issues concerning micro-scale properties of elemental and III-V compound semiconductors, in particular, the problems associated with native defects, dopants, and unintentional impurities in these materials. It provided a comprehensive understanding of light / matter interactions in optical microcavities and non-linear semiconductors. It covered central areas of the epitaxial semiconductor research and technology, including layer growth for advanced optoelectronic devices, and the fabrication and studies of performance characteristics of the devices, and integration of the devices with optical fibre components.

The Consortium published 124 refereed journal articles and 89 (contributed) papers in international conferences. The number of monographs, invited review articles, and plenary or invited talks in international conferences totalled 31, and 4 patent applications were filed. 15 PhD degrees, 1 Licentiate degree, and 28 Master degrees were produced in part or in whole within MACOMIO.

The Partners participated in a number of international (and national) research projects. Those relevant to MACOMIO were the ψ_k Network, the COST P3 and COST-268 Activities, STRUC Programme of the European Science Foundation, Nordic Network NOCDAD supported by the NorFA foundation, the EU ESPRIT SMILED Programme, the EU FALCON Network, and the EU Marie Curie Doctoral Training Programme. The international visibility and international relations were further accentuated by Partners' co-operation with tens of university groups and companies worldwide.

The Academy of Finland allocated FIM 6.199 million (€1.043 million) to the project. When support from external sources is taken into account the total budget of MACOMIO amounted to FIM 12-14 million (€ 2.0 – 2.4 million).

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[16] Department of Electronics (TUT 2), Tampere University of Technology
[17] Laboratory of Physics (HUT 1), Helsinki University of Technology

1 Partners and Funding

1.1 ORC / TUT 1. Research Staff of the Optoelectronics Research Centre (ORC), Tampere University of Technology

Name	Degree	Job Title	Sex
Pessa Markus	Professor	P. I. of TUT1	M
Bezotosnyi Viktor	PhD	Senior Researcher	M
Haapamaa Jouko	PhD	Senior Researcher	M
Li Wei	PhD	Senior Researcher	M
Savolainen Pekka	PhD	Researcher	M
Uusimaa Petteri	PhD	Researcher	M
Xiang Ning	PhD	Researcher	F
Laukkanen Pekka	M.Sc.	Researcher	M
Lehkonen Sami	M.Sc.	Researcher	M
Lindfors Jukka	M.Sc.	Researcher	M
Pavelescu Emil	M.Sc.	Researcher	M
Rintamöykky Ari	M.Sc.	Researcher	M
Toikkanen Lauri	M.Sc.	Researcher	M
Tukiainen Antti	M.Sc.	Researcher	M
Turpeinen Jani	M.Sc.	Researcher	M
Vainionpää Anne	M.Sc.	Researcher	F
Hirvonen Ilkka	Undergraduate student	Research Assistant	M
Hänninen Ismo	Undergraduate student	Research Assistant	M
Isomäki Antti	Undergraduate student	Research Assistant	M
Karjalainen Päivi	Undergraduate student	Research Assistant	F
Leinonen Tomi	Undergraduate student	Research Assistant	M
Suni Jarmo	Undergraduate student	Research Assistant	M
Suomalainen Soile	Undergraduate student	Research Assistant	F
Suominen Mikko	Undergraduate student	Research Assistant	M
Viheriälä Jukka	Undergraduate student	Research Assistant	M

1.2 TUT 2. Research Staff of the Department of Electronics, Tampere University of Technology

Name	Degree	Job Title	Sex
Ristolainen Eero	Professor	P.I. of TUT2	M
Karvonen Anna	M.Sc.	Researcher	F
Alander Tapani	M.Sc.	Researcher	M

1.3 HUT 1. Research Staff of the Laboratory of Physics, Helsinki University of Technology

Name	Degree	Job Title	Sex
Saarinen Kimmo	Professor	P.I. of HUT1	M
Dekker James	PhD	Senior Researcher	M
Slotte Jonatan	PhD	Senior Researcher	M
Oila Juha	Postgraduate student	Researcher	M
Ranki V.	Postgraduate student	Researcher	M
Laakso Antti	Postgraduate student	Researcher	M
Nissilä Jaani	Postgraduate student	Researcher	M
Aavikko Reino	Student	Research Assistant	M
Pelli Antti	Student	Research Assistant	M
Hautakangas Sami	Student	Research Assistant	M

1.4 COMP / HUT 2. Research Staff of COMP / Laboratory of Physics, Helsinki University of Technology

Name	Degree	Job Title	Sex
Nieminen Risto	Professor	P.I. of HUT2	M
Juhani von Boehm	Professor	Senior Researcher	M
Martti Puska	Professor	Senior Researcher	M
Mikko Hakala	Post-doctoral fellow	Researcher	M
Markus Kaukonen	Post-doctoral fellow	Researcher	M
Young-Joo Lee	Post-doctoral fellow	Researcher	M
Juha Lento	Post-doctoral fellow	Researcher	M

Tomi Mattila	Post-doctoral fellow	Researcher	M
Marko Pesola	Post-doctoral fellow	Researcher	M
Sami Pöykkö	Post-doctoral fellow	Researcher	M
Torsten Staab	Post-doctoral fellow	Researcher	M
Leena Torpo	Post-doctoral fellow	Researcher	F
Petri Lehtinen	Undergraduate student	Research Assistant	M
Ville Sammalkorpi	Undergraduate student	Research Assistant	M

1.5 UH. Research Staff of the Department of Physics, Accelerator Laboratory, University of Helsinki

Name	**Degree**	**Job Title**	**Sex**
Keinonen Juhani	Professor	P. I. of UH	M
Rauhala Eero	Ph.D.	Researcher	M
Kai Nordlund	Ph.D.	Researcher	M
Ahlgren Tommy	Ph.D.	Researcher	M
E.Vainonen-Ahlgren	Ph.D.	Researcher	F
Pusa Petteri	M.Sc.	Researcher	M
Szabolcs Galambosi	M.Sc.	Researcher	M
Janne Nord	M.Sc.	Researcher	M
Jarkko Peltola	M.Sc.	Researcher	M
Kenichiro Mizohata	M.Sc	Researcher	M
Jura Tarus	Ph.D.	Researcher	M
Jarkko Peltola	M.Sc.	Researcher	M
Timo Sajavaara	M.Sc.	Researcher	M
Anna Ruhala	M.Sc.	Student	F

1.6 VTT. Research Staff of the Chemical Technology, VTT Processes, Technical Research Centre of Finland

Name	**Degree**	**Job Title**	**Sex**
Likonen Jari	Professor	P.I. of VTT	M
Lehto Sari	Ph.D	Senior Researcher	F

1.7 Funding

Table. Funding of the project in 1000 FIM in 1999-2002. Internal funding consists of manpower costs and operational expenditures* provided by the organisation. The funding provided by the Academy of Finland and other external sources** is also shown in the table.

Partner	Funding	1999	2000	2001	2002	**Total**
ORC / TUT1	ORC / TUT	150	250	250	150	**800**
	Academy	176	1155	863	406	**2 600**
TUT2	TUT					
	Academy	54	163	83	-	**300**
HUT1	HUT	50	400	400	100	**950**
	Academy	50	412,5	406,5	131	**1 000**
COMP / HUT2	HUT	200	220	250	250	**920**
	Academy	73	353	343	230	**999**
	Other (EU, industry, foundations)	250	400	400	400	**1 450**
UH	UH	200	250	250	100	**800**
	Academy	186	281,5	243	89,5	**800**
VTT	VTT	37	207	182	74	**500**
	Academy	37	207	182	74	**500**
Total		**1 463**	**4 299**	**3 852,5**	**2 004,5**	**11 619**

*Operational expenditures are not necessarily included in the internal funding; the accounting practice varies from one Partner to another.

** During the project the Partners have invested in new research equipment, paid from external sources, but this money may not have been included in the table. For example, the major investments of ORC in measurement instruments, worth € 770'000, is excluded here.

2 Research Work

2.1 Objectives and Work Plan

ORC / TUT 1 The key objective was to obtain a comprehensive understanding of interactions between light and matter in a new class of semiconductors (dilute nitrides) and in optical microcavities and to exploit this knowledge to develop advanced optoelectronic devices and systems. Other objectives aimed at providing information about (i) the nature of microscopic defects in semiconductors, (ii) design and growth of device structures of interest, (iii) fabrication processes and performance characteristics of the devices, and (iv) integration of the devices with optical fibre components

ORC was also expected to assess the viability of the materials and technologies developed in this project for industrial applications.

On the management side, ORC was responsible for overall co-ordination of MACOMIO, arranging and chairing the meetings, and overall technical reporting.

TUT 2 The aim was to apply the direct packaging – flip chip – technique and ultra-high-speed circuits for driving semiconductor lasers.

HUT 1 The role of HUT 1 involved basic experimental research on the electron and atomic structure of deep and shallow centers in GaN based materials. The objective of the work was to understand the role of lattice defects and impurities on the electrical and optical properties of GaN. This included (i) the influence of doping on the formation of point defects, (ii) the electrical deactivation of *n* and *p*-type doping, (iii) metastability of defects, (iv) optical properties of defects: absorption and luminescence, (v) the stoichiometry of growth conditions and the formation of point defects in GaN films, and (vi) the influence of the substrate material on the point defects in GaN layers and the defects at the layer/substrate interface. The results obtained by HUT 1 could also be utilized as a feedback to ORC in the optimisation of the growth conditions of GaN.

COMP / HUT 2 The general objective was to develop and apply powerful theoretical and large-scale computational methods to model the semiconductor materials and structures relevant for microelectronic and optoelectronic device applications. The basic strategy was to use a multi-scale approach, which means that results obtained first at the microscopic (*i.e*. atomistic) level were used to model meso-scale (*i.e*. nanometer to micrometer) and eventually also macro-scale phenomena.

The micro-scale properties necessitate the use of quantum physics methods, such as the density-functional theory widely applied in electronic-structure and total-energy calculations. Meso-scale phenomena were in turn approached via molecular-dynamics and kinetic Monte Carlo simulations for such processes as atomic migration. Finally, continuum equations such as those derived from rate-equation theory were used to model macro-scale phenomena, such as long-time annealing of defect-related phenomena.

Problems of particular interest in this project were those associated with native defects, dopants, and unintentional impurities in novel semiconductor materials and structures made thereof. These were closely related to the practical growth of both thin-film and bulk materials, using different techniques (such as epitaxial growth or Czochralski-type processing). In real materials, defects always appear at concentrations, which have a strong influence on the electronic properties of the semiconductor materials. The appearance of defects needs to be correlated with the growth conditions in order to optimise the growth of materials and structures with desired properties.

Unlike in silicon, the question of controlled doping (*n*-type or *p*-type) in compound semiconductors is still largely an unsolved problem with crucial consequence for the manufacture of quantum devices. The factors limiting doping efficiencies need to be understood at the atomistic level, which requires quantitatively accurate calculations. Dopants usually interact strongly with native defects and unintentional impurities (such as hydrogen and oxygen), which makes the situation very complex. First-principles quantum calculations must be carried out to resolve the influence of complex formation in doping behavior.

Several experimental techniques are nowadays available for the study of atomic-scale defects in semiconductors. However, these techniques are indirect and require sophisticated modelling in their proper interpretation. For example, the positron techniques used in this project must be complemented by detailed calculations for the annihilation parameters in order to obtain unambiguous fingerprints from the experimental studies. An important objective of our work has thus been to provide theory support for the defect characterisation using positron techniques and other probes.

UH UH's part of the MACOMIO project aimed to (i) characterise the nature of defects and strain states in the semiconductor materials studied, and (ii) utilize ion beam methods to modify and produce optoelectronic semiconductor materials and produce standards for collaborating partners.

Project work plan included (a) characterisation of atomic structures at the surface and in the bulk, concentration depth distributions of impurities and defects and their behaviour upon annealing, a study of crystal quality and location of lattice sites of foreign and host atoms, (b) atomistic simulations of irradiation effects, strain fields, mechanical and defect properties, dopant distributions and location of foreign atoms, and (c) production and testing of standards for other parties in the collaboration.

VTT The main role was to apply the secondary ion mass spectroscopy (SIMS) to determine concentrations of impurities and compositional profiles of semiconductors.

2.2 Progress Report: Common Themes

The progress was reviewed in three Workshops, as scheduled in the Project Plan, corresponding to major milestones and corresponding to the point in time at which Deliverables were scheduled.[18] In the Workshops, all pertinent administrative issues were also addressed. In addition, Partners held smaller meetings when necessary to clarify details of the workparts and plan for the joint tasks.

The Academy of Finland organised two general meetings on EMMA.

The co-operation between the Partners was useful. It resulted in 14 joint papers published in the refereed journals, representing over 10 % of all the journal articles produced.

ORC invested € 770'000 from its own budget in research equipment during the project. This remarkable extra support to MACOMIO helped people carry out expensive, technologically oriented workparts.

Besides co-operation with a large number of university groups, co-operation with about 20 companies also contributed favourably to accomplishments of the tasks.

The excellent results obtained in MACOMIO paved the way for the establishment of a new company, the second spin-off in the field of epitaxial compound semiconductors in Finland. The two companies, already representing remarkable investment with estimated revenues of € 14 - 18 million in 2002, may be the biggest industry ever resulted from the basic research of physical sciences in Finland.

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[18] Proceedings of the Workshops 1, 2, and 3 are available at ORC on request in the form of viewgraph booklets

2.3 Progress Report: Progress by ORC

2.3.1 Materials

$Ga_{1-x}In_xN_yAs_{1-y}$ for wavelengths $1.3 < \lambda < 1.55$ µm

Increasing evidence brought up in the past few months indicates that a new class of semiconductors, $Ga_{1-x}In_xN_yAs_{1-y}$ ($0 < y < 5$ %), which in fact were discovered ten years ago but drew little attention in the 90's, are promising materials for lasers. Because GaInNAs is closely lattice-matched to GaAs, the cost-effective GaAs technology could be extended to the telecom wavelengths 1.3 – 1.55 µm for the first time.

Our studies have revealed surprising intrinsic properties of GaInNAs. The observations suggest that controlling growth of $Ga_{1-x}In_xN_yAs_{1-y}$ / GaAs quantum wells (QW's) is even more difficult than what has been reported in the literature.

We worked in close co-operation with UH, HUT 1, COMP / HUT 2, and VTT on this novel semiconductor, using positron annihilation measurements, secondary ion mass spectroscopy (SIMS), a nuclear reaction analysis in conjunction with Rutherford backscattering, XRD, and photoluminescence (PL). We could show that $Ga_{1-x}In_xN_yAs_{1-y}$ contains a high density of interstitial nitrogen (10^{19} cm^{-3}) and Ga vacancies (10^{16} cm^{-3}). Interstitial nitrogen was removed by rapid thermal annealing (RTA), which improved PL intensity by one or two orders of magnitude, but caused an undesired blue shift. The measured and calculated X-ray diffraction from the QW's indicated that the blue shift of PL upon RTA was due to Ga / In / N interdiffusion.

However, diffusion may not be the only phenomenon causing spectral shifts, as temperature is varied. Recently it was predicted[19] that GaInNAs exhibits several different bandgaps at fixed compositions x and y. The theory predicts that "random" GaInNAs contains atomic clusters of type $N\text{-}In_mGa_{4-m}$ ($0 \leq m \leq 4$) with N acting as an isovalent trap. The clusters would have five different energy states m above the conduction band minimum, pushing the band edge downwards by a repulsion mechanism. The change in alloy bandgap depends on the distribution of clusters with different m values. To study this problem, we prepared GaInNAs / GaNAs / GaAs QW samples at different growth temperatures, but kept other growth parameters constant. No change in QW composition was found by XRD. Yet, the PL peak was *red-shifted*, as growth temperature was increased (growth temperature was much lower than that in RTA treatment). At the same time, the PL peak was broadened and potential-energy fluctuations at the band edge were increased, while peak intensity was dramatically decreased. These preliminary observations, made in the last month of MACOMIO (June 2002), lend qualitative support to predicted cluster effects: In-ligand rich sites of N change for Ga-ligand rich sites, which cause a red shift, a decrease in intensity, and an increase in potential energy fluctuations according to the theory.

$Ga_{1-x}In_xN$ for $\lambda < 450$ nm

$Ga_{1-x}In_xN$ operating in the blue - UV range has enormous market potential in lightening (white LEDs), traffic lights, etc. The Partners of this project have studied MBE-grown $Ga_{1-x}In_xN$

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[19] K. Kim and A. Zunger, Phys. Rev. Lett. **86**, 2609 (2001)

materials, applying an extensive set of characterisation methods to explore electrical, optical, and defect properties.

Si-doped GaN samples were grown on GaN / sapphire templates by MBE. The analyses of these samples showed that some Si donors remained deactivated at high doping concentrations. Simultaneously, undesired yellow luminescence increased with Si doping. Positron annihilation experiments of HUT 1 suggested that the defects might be attributed to Ga vacancy clusters and possibly Ga monovacancies. It was also found that there were other defects that left their fingerprints in the positron annihilation data, and they could be due to Ga – donor complexes.

Judging from the results obtained for MBE-grown large-bandgap nitrides of this Section and small-bandgap nitrides of previous Section, one could conclude that alloying nitrogen with Ga-based semiconductors always generates point-like defects, which either deteriorate or completely suppress light emission from the III-N's. On the other hand, judging from performance characteristics of nitride-based devices, discussed later, one could say that the MBE method is not competitive for growth of GaInN with respect to metal-organic chemical vapour deposition (MOCVD), but it is very competitive for growth of GaInNAs at long wavelengths.

2.3.2 Photons in a microcavity

Light emitting sources with the vertical geometry have a short Fabry-Perot (F-P) microcavity, three orders of magnitude shorter than the cavity of edge-emitting devices. The microcavity, containing QW's as photon generators, is sandwiched between two distributed Bragg reflector (DBR) stacks to cause light bouncing back and forth for amplification. The interaction between the cavity and the DBRs supports a single longitudinal optical cavity mode (CM) *via* destructive interference between the reflected light from the bottom and top DBRs, creating a sharp dip in the reflectivity (R) spectrum at the cavity wavelength λ_{CM}. This wavelength should be approximately aligned with respect to the wavelength of the QW ground-state transition λ_{QW}. The external quantum efficiency (η) is largely enhanced by the cavity effect, in particular, if the two wavelengths are appropriately "detuned": $\lambda_{QW} < \lambda_{CM}$.

We have studied interplay between the cavity mode and the QW exciton mode by applying a very accurate method, photo-modulated reflectance (PR), to probe light originating from a one-dimensional "optical trap". This work was done in co-operation with the University of Surrey, UK. The R spectrum gives information about the structure of the DBRs and the cavity, showing the position and shape of the CM dip, but provides no information about the quantum well. Traditional techniques, such as front-surface photo-luminescence or electro-luminescence give misleading results for λ_{QW}, due to the modification of front-emission spectrum by the R spectrum of the DBR. By contrast, the PR spectroscopy, applied in this work yields information about both λ_{CM} and λ_{QW}. PR is the only known non-contact, non-destructive method of doing so.

Angle- and temperature-dependent PR method was applied to AlGaInP / GaAs QW resonant-cavity spontaneous light emitters (RC-LEDs) oscillating at 650 - 660 nm. Prominent signals were observed from the F-P mode, excitonic transitions, and higher-order transitions. The cavity / exciton resonance could be determined accurately, which is of great importance when designing vertical cavity light emitters.

It is more difficult to confine photons than electrons in a quantum mechanical "box". The photons leak out of the box into the confining mirrors, due to a small index difference (Δn) between the adjacent layers in the DBR, which translates into the formation of a large effective cavity length (L_p).[20] A simple calculation[20] shows that L_p becomes about four times larger than the physical cavity (L_0) at 650 nm, leading to weak cavity / exciton coupling. In fact, it is never possible to achieve enhancement in intensity by a factor of ten, as predicted by theory for a thin F-P cavity with ideal DBRs.[21] By the same token, InP VCSELs at 1.3 μm are extremely difficult to make; one needs GaInNAs on GaAs to prepare a monolithic 1.3-μm VCSEL. Much better photon confinement, of course, could be obtained with the aid of photonic bandgap crystals.

Fig. 1 illustrates an optical field distribution, calculated within the transfer matrix formalism for a real 650-nm RC-LED structure. Photons are captured by the cavity, but the tail of the field penetrates into the bottom mirror. The field drops down to 1/e of its cavity value at $L_p \approx 600$ nm with respect to the QW centre, consistent with the penetration length estimate.[20]

In summary, this workpart has given us information about the properties of light originating from a microcavity and the ways of measuring such light. Cavity enhancement in actual structures remains lower than what is predicted by theory for an ideal case, which is unavoidable because of weak cavity / QW coupling in the visible spectra where no monolithic DBR with large Δn is possible. However, the extraction quantum efficiency, as shown later, is much higher – and dynamic properties are enhanced in accordance with the theory of cavity quantum electrodynamics – for the microcavity structures than for conventional ones.

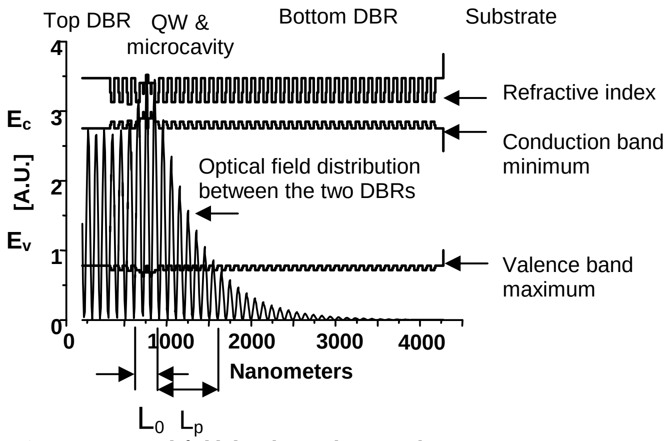

Figure 1. Optical field distribution between the two DBR mirrors, refractive index, and the conduction band minimum and valence band maximum. In this example, the microcavity contains 3 quantum wells.

2.3.3 Development of device process technology

One of the goals was to learn controlling chemical processes in wet thermal oxidation of $Al_zGa_{1-z}As$, which is applied to create a current aperture layer in vertical cavity components. This work

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[20] The penetration depth is given by $L_p = \frac{\lambda}{2n}\Delta m_c \approx \frac{\lambda}{4\Delta n}$ where $m_c = m_0 + \Delta m_c$ is the effective cavity order with $m_0 = 2nL_0/\lambda$ (the bare cavity order, m_0 = 2 for a usual cosine-type one-λ cavity) and $\Delta m_c = \frac{n_h n_l}{2n_{ave}\Delta n} \approx \frac{n}{2\Delta n}$. Typically $n \approx 3.5$ and $\Delta n \approx 0.3$, which for a symmetric cavity gives $L_p \approx 540$ nm at $\lambda = 650$ nm, or $m_c \approx 4\, m_0$.

[21] G. Björk *et al.,* Phys. Rev. **A44**, 669 (1991)

was done, in part, in co-operation with eight research groups of a EU COST-268 Project. As a result, optimal oxidation conditions were found. The oxidation rate in the lateral direction was found to be a function of z: for a reasonable rate one needs z > 98 %. For the layers used in actual devices the oxidation rate depended linearly on oxidation time to a depth of 10 - 15 μm (in the lateral direction), upon which it became less controllable.

Another work related to device processing concerned optimisation of lithographic masks. This work resulted in (i) new exit-window masks that reduced shading effects of metal fingers and decreased "current crowding", and led (ii) to an intracavity contact design. Using intracavity contacts, the top and bottom DBRs can remain undoped. The undoped mirrors have two desired features: they reduce absorption of light, and allow AlAs / GaAs layers to be used in DBRs with maximal Δn, which translates into broad, high-*R* stop-bands with a fewer layers.

2.3.4 Devices

The first device to be discussed is a 650-nm RC-LED, developed in MACOMIO and in two other projects: Tekes POLAR and EU Esprit SMILED in 1999 – 2001. The RC-LED represents novel light emitters, the characteristics of which are in between those of VCSELs and conventional LEDs. They may be suitable for medium-speed PMMA polymer optical fibre (POF) data communications systems and possibly micro-displays. ORC has demonstrated RC-LEDs at the data transmission window of 650 nm of POF, with the maximum external quantum efficiency η of 9.5 %, which is close to the theoretical limit of $\eta \approx 11$ % (*cf.* $\eta \approx 2$ % for a usual LED). The modulation bandwidth (f_{-3dB}) is around 200 MHz for $^{\varnothing}$84-μm device and record 350

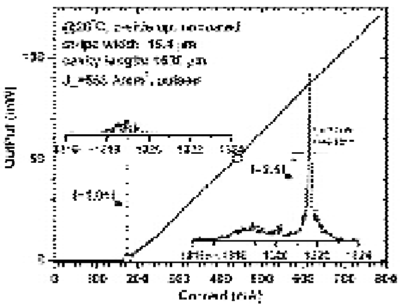

Figure 2. GaInNAs single-QW laser: the L-I curve and the spectra at and above the threshold drive current.

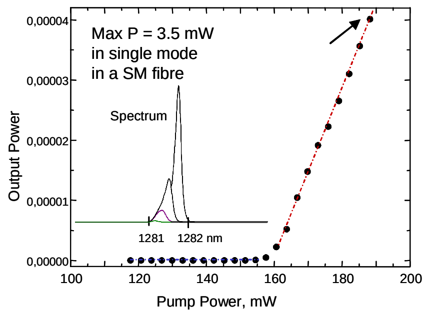

Figure 3. GaInNAs 15-QW VCSEL, optically pumped, launching 3.5 mW output in single mode into a single mode fibre.

MHz for $^{\varnothing}$40-μm device, way higher than that of a simple LED. The experiments show that a 250 Mbit/s data transmission rate is possible for a standard 20-m long step-index POF and as high as 622 Mbit/s for a 1-m long POF using the RC-LED. The output power is typically 1-2 mW for the $^{\varnothing}$84-μm device, while power levels up to 15 mW have been demonstrated for a $^{\varnothing}$500-μm device.[22]

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[22] M. Pessa, *et al:*. Topical Review: Semicond. Sci. Technol. **17,** R1-R9 (2002).

The second device ORC developed was a GaInNAs-based edge-emitting laser. This laser was one of the first of its kind in Europe (in Sept. 2001). The output power is 120 mW in pulse mode and 40 mW in cw mode. The threshold current density is relatively low, 563 A/cm^2, and the wavelength is over 1.3 μm (Fig. 2).

We also demonstrated a monolithic, optically pumped GaInNAs VCSEL containing a 15-QW structure (Fig. 3). This device launches 3.5 mW output in single mode into a single mode fibre, when pumped by a 980-nm diode laser at the power level of 190 mW. To the best of our knowledge, this is the highest fibre-coupled single-mode power reported on GaInNAs VCSELs to date.

2.3. 5 Semiconductor saturable absorber integrated with a fibre laser

Another device developed was a vertical structure InP-based, non-linear semiconductor saturable absorber mirror (SESAM) having up to 42 quantum wells deposited onto a DBR at 1.55 μm. The SESAM was used as an external cavity mirror in connection with a rare-earth-doped fibre laser to generate mode-locked, self-initiated ultra-short light pulses. The SESAM was monolithically grown on InP and it employed a Burstein-Moss-shifted GaInP / InP DBR to reduce absorption. The pulse length was around 200 fs, which is among the shortest pulses ever demonstrated at the telecom wavelength. Exploiting a colliding pulse configuration the SESAM performed a dual function: (i) pulse shaping and (ii) stabilisation of the repetition rate. Also, harmonic pulse train synchronisation to an external signal was demonstrated by directly modulating the 980-nm diode pump, which provided gain and optical modulation of the SESAM.

This success has led to extensive research and development of various devices based on the SESAM strategy now available at ORC. Some of these devices have already been optimised and used in specific applications, such as ultrashort pulse generation, dispersion compensation, and noise suppression in fibre optical amplifiers. Experience acquired in this and other projects allows us to combine the optical fibre technology with the advanced semiconductor technology for potential applications in tomorrow’s ultra-fast telecommunications.

2.4 Progress Report: Progress by TUT 2

TUT 2 studied direct packaging (flip-chip) of high-speed drivers for semiconductor lasers. VCSEL driver circuits for optical fibre communications were designed and measured. Processing the drives was carried out by Austria Mikro Systeme International (AMS) using a 0.8-μm SiGe (BYR) technology offered by Europractice IC Service. The lasers were flip-chip joined by TUT 2 either to board or driver circuitry. The driver circuits were tested without lasers, achieving the speed of almost 20 GHz. The joined laser-driver package has not yet been tested, but no fundamental problems are expected in the coming tests.

2.5. Progress Report: Progress by HUT 1

The role of positron group has been in the characterization of deep and shallow levels in GaN and related compounds. The main results can be summarized as follows.

Positron experiments detect Ga vacancies as native defects in GaN bulk crystals. The concentration of V_{Ga} decreases with increasing Mg doping, as expected from the behavior of their formation energy as a function of the Fermi level. The trapping of positrons at the hydrogenic state around negative ions gives evidence that most of the Mg atoms are negatively charged. This suggests that Mg doping converts n-type GaN to semi-insulating mainly due to the electrical compensation of O_N^+ donors by Mg_{Ga}^- acceptors.

Ga vacancies are observed as native defects in various n-type GaN overlayers grown by MOCVD or MBE on sapphire or GaN substrates. Their concentration is > 10^{17} cm^{-3} in nominally undoped material, which show n-type conductivity due to residual oxygen. When similar doping is done with Si impurities and less oxygen is present, the concentration of Ga vacancies is lower by at least an order of magnitude. No Ga vacancies are observed in p-type or semi-insulating layers doped with Mg. These trends agree well with the theoretical calculations, which predict that the formation energy of Ga vacancy is high in p-type and semi-insulating material, but greatly reduced in n-type GaN, and even further reduced due to the formation of V_{Ga} - O_N complexes.

In addition to doping, the presence of open-volume defects in GaN layers depends on the growth conditions. The concentrations of Ga vacancies increase strongly when more N rich stoichiometry is applied in the MOCVD growth. On the other hand, the lattice mismatch and associated dislocation density seem to have less influence on the formation of point defects than doping and stoichiometry – at least at distances > 0.5 μm from the layer/substrate interface. This suggests that the formation of point defect in both epitaxial layers and bulk crystals follows mainly the trends expected for defects in thermal equilibrium.

2.6 Progress Report: Progress by COMP / HUT 2

The research work carried out at COMP (HUT 2) has contributed to three common themes in the project. These are:

(i) Atomistic studies for a large number of defect/impurity complexes studied experimentally by different characterisation techniques, using samples prepared by the growth techniques developed in the project;

(ii) Calculations of basic materials/electronic characteristics (i.e. band offsets in heterostructures) for relevant structures; the systematic study of diffusion and long-term annealing mechanisms relevant for thermal processing of as-grown and/or as-implanted materials;

(iii) Development of computational techniques for interpretation of experiments, especially for fingerprinting defect structures based on positron-annihilation experiments.

Here we give a short summary of the main results obtained in the project, concentrating on the applications of theoretical and computational modelling to the actual materials problems. Less attention is paid to the ongoing development of new theoretical tools and computational techniques, which is an integral part of our activity as well.

Our work in computational materials science is widely recognised, both nationally and internationally. A sign of the national recognition is the status of COMP as a Center of Excellence designated by the Academy of Finland for 2000-2005. An example of the international recognition is the large number of invited talks given by COMP members at international conferences. Related to this project, we have given 11 invited and plenary talks at international conferences during 1999-2002.

2.6.1 Interface structures and band offsets at heterojunctions

The atomic-scale structure at interfaces between two compound semiconductor phases (often ternary or even quaternary alloys) is an important question, as determines the band offsets for carriers in the device. Using powerful plane-wave pseudopotential techniques, we have obtained the equilibrium (i.e. lowest-energy) atomic structures for compound semiconductor interfaces,[23] [24] and compared the results with experimental investigations. This work has been carried out in collaboration with the ORC group.

2.6.2 Metastable defects and interstitials in GaAs

GaAs exhibits the important phenomenon of metastability, associated with the so-called EL2 defect. The atomistic interpretation of the EL2 defect is generally the accepted to be the As antisite (As_{Ga}). However, there are in fact several EL2-type defects with slightly different experimental characteristics. We have studied possible atomistic models for the EL2 family, including pairs of antisites.[25]
In a related study [1], we have demonstrated that the experimentally observed strain in low-temperature grown GaAs is due to As antisites rather than interstitials. This work has been carried out in collaboration with HUT 1.

2.6.3 Development of a robust computational method for Doppler-lineshape-positron spectroscopy

The development of the coincidence measurement method has made the Doppler-lineshape measurement an important high-resolution tool for identifying the atomistic environment of defects in materials. The proper interpretation of the measured lineshape requires a quantitative computational technique for the electron-positron momentum density, which we have developed and applied[26] [27] and Ref. [2]. This work has been carried out in collaboration with HUT 1.

2.6.4 Native defects in silicon carbide

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[23] F. Bernardini and R.M. Nieminen, Phys. Rev. B **55**, 1718 (1997)

[24] A. Lindel, M. Pessa, A. Salokatve, F. Bernardini, R.M. Nieminen, and M. Paalanen, J. Appl. Phys. **82**, 3374 (1997)

[25] S. Pöykkö, M.J. Puska, and R.M. Nieminen, Phys. Rev. B **55**, 6914 (1997)

[26] B. Barbiellini, M. Hakala, M.J. Puska, R.M. Nieminen, A.A. Manuel, Phys. Rev. B **56**, 7136 (1997)

[27] M. hakala, M.J. Puska, R.M. Nieminen, Phys. Rev. B **57**, 7621 (1998)

Silicon carbide is an important semiconductor material, whose controlled growth and doping are still quite problematic. It is also an important substrate material for III-nitrides. In a series of papers, we have carried out a systematic study of the properties of native defects in various polytypes of SiC. These include vacancies in both sublattices, antisites, and divacancies[28] and Refs. [3, 4, 5, 6].

2.6.5 Point-defect complexes, doping and broadband luminescence in nitride semiconductors

By using large-scale electronic structure calculations, we have demonstrated the role of unintentional impurities (oxygen, silicon in particular) in as-grown Gan and AlN.[29] We are now completing a comprehensive summary of the theoretical investigations of doping, defects and growth of BN, AlN, GaN and InN [7]. This work has been carried out in collaboration with HUT 2, UH and ORC.

2.6.6 Oxygen and boron in silicon

We have studied extensively the properties of oxygen in silicon, dissolved from the quartz crucible into the material during the Czochralski growth from molten silicon. large-scale electronic structure and total-energy calculations have been carried out to obtain the properties of oxygen complexes ranging from single interstitials to chains of up to 15 oxygen atoms. The fingerprinting of these complexes has been made through calculations of both their electronic properties (donor character, metastability) and vibrational properties, experimentally accessible via Raman and IR techniques. The migration barriers for moving oxygen complexes have been calculated through detailed mapping of the potential energy hypersurfaces. Kinetic equations describing the possible migration, association, dissociation and restructuring processes of moving oxygen clusters have been solved. This enables a detailed study of the annealing kinetics of thermal double donors, which we can unambiguously associate with the various chain structures. This work solves many long-standing problems associated with thermal-donor kinetics, and has been described in detail in a number of publications[30] and Refs. [8-14, 23, 24]. Boron is implanted as a dopant in silicon structures. Implantation produces defects (vacancies and interstitials), which interact with the moving boron during thermal treatment. The mechanisms responsible for the transient-enhanced diffusion (TED) processes associated with dopant implantation are still widely debated.. To elucidate the properties of boron migration in silicon, we have carried out detailed first-principles molecular dynamics simulations of its motion [16].

2.6.7 Self-diffusion in GaSb

Diffusion studies in isotopically enriched GaSb have revealed a striking anisotropy between the motion of atoms in the two sublattices. We have carried out a computational study, which shows that the dominant defects are the Ga vacancy and the Sb interstitial. Vacancies in the Sb

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[28] L. Torpo, S. Pöykkö, R.M. Nieminen, Phys. Rev. B**57**, 6243 (1998)

[29] T. Mattila, R.M. Nieminen, Phys. Rev. B **55**, 0571 (1997)

[30] M. Pesola, J. von Boehm, S. Pöykkö, R.M. Nieminen, Phys. Rev. B **58**, 1106 (1998)

sublattice are not stable. This gives rise to natural explanation of the self-diffusion as due to the vacancy mechanism in the Ga sublattice [17].

2.6.8 Development of new computational techniques

The supercell method is a powerful technique for large-scale electronic structure calculations of defects and other low-symmetry systems. However, the supercell size has to be large enough in order to avoid spurious interactions between defects in neighbouring supercells. While the technique is widely used, the convergence issue as a function of the supercell size has not been adequately addressed earlier. We have published a systematic study of the convergence,[31] and shown also how to avoid spurious effects due to the insertion of aneutralizing background charge, necessary to handle charged defects [19]. The ensuing Madelung-type correction depends also on the supercell size, and can be substantial, especially for highly charged defects.

We have also developed a new, efficient method to locate migration paths and transition states for dynamical simulations [19]. This technique enables long-time simulations of rare events in a complex potential energy landscape.

2.7 Progress Report: Progress by UH

2.7.1 Introduction

Identification of vacancy charge states in diffusion of arsenic in germanium [4]

The increasing importance of Ge in applications reported in the literature, such as $Si_{1-x}Ge_x$ devices and multi-junction GaAs/Ge and GaInP/GaAs/Ge solar cells showed that further studies on dopant diffusion in Ge is needed to understand the diffusion mechanisms. It was reported that during growth of a GaAs layer on Ge a junction was created through the in-diffusion of Ga and As, resulting in a two-junction tandem cell. Later on this process has been used to create n-type layers in Ge.

To study why this two-junction is created, GaAs deposition on Ge was done by molecular beam epitaxy at ORC and annealing were carried out using rapid thermal annealing ex-situ in pure N_2 atmosphere, in the temperature range from 500 to 800 ^oC. The diffusion of As into Ge from a GaAs overlayer deposited on a p-type Ge substrate was monitored by secondary ion mass spectrometry (SIMS). Figure 1 shows the resulting depth profiles of Ga and As in Ge.

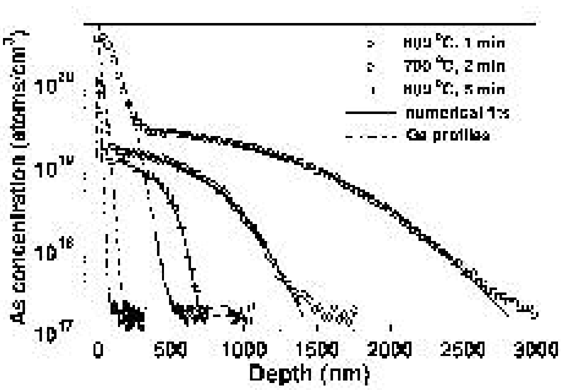

Figure 1. Concentration profiles of As and Ga obtained in SIMS measurements for samples annealed at 600, 700, and 800 ^oC. The numerical fits are calculated for the charge states 0 and 2- of Ge vacancies.

[31] M.J. Puska, S. Pöykkö, M. Pesola, R.M. Nieminen, Phys. rev. B **58**, 1318 (1998)

A concentration-dependent diffusion of As atoms was observed. The concentration dependence is explained by a Fermi-level-dependent diffusion model:

(1) $$\frac{\partial C_{As}}{\partial t} = \frac{\partial}{\partial x}\left(D_{As}{}^{eff} \frac{\partial C_{As}}{\partial x} \right)$$

where C_{As} is the concentration of As atoms, x the depth, and t diffusion time. $D_{As}{}^{eff}$ is the effective As diffusion coefficient:

(2) $$D_{As}{}^{eff} = D_{As}{}^{0} + D_{As}{}^{1-}\left(\frac{n}{n_i}\right) + D_{As}{}^{2-}\left(\frac{n}{n_i}\right)^2$$

where $D_{As}{}^{n}$ are diffusions through different charge states and n and ni the extrinsic and intrinsic free electron concentrations, respectively.

Arsenic atoms are shown to diffuse through Ge vacancies with the charge states 2- and 0. No presence of the singly negatively charged vacancies was observed, indicating that Ge vacancy could be a negative U-center.

Concentration of interstitial and substitutional nitrogen in GaN_xAs_{1-x} [24]

The rapid development of optoelectronics devices, especially at wavelength range of 1.3 - 1.55 µm, has focused the research toward Ga(In)Nas alloys, where a small amount of N leads to considerable band gap reduction due to the large band gap bowing. Incorporation of N into Ga(In)As deteriorates the crystalline quality. The origin for this has received a lot of attention but was not explained in the literature.

The purpose of our study was to experimentally determine the concentrations of interstitial and substitutional N as a function of mean N concentration and temperature. This information is indispensable for N diffusivity calculations where the ratio between interstitial and substitutional atoms is needed and for understanding the effects of rapid thermal annealing (RTA) on Ga(In)NAs structures.

To study why incorporation of N into GaAs makes the crystal quality worse, GaNAs films with mean nitrogen concentrations between 0.3 and 3 at.% were grown by a gas-source molecular-beam epitaxy system at the Tampere University of Technology.

The N concentration measurements were done by secondary ion mass spectrometry (SIMS), and time-of-flight elastic recoil detection analysis (TOF-ERDA) with the 5-MV tandem accelerator EGP-10-II of the University of Helsinki. For the ^{14}N concentration and GaAs channeling measurements, beams of 1.3 MeV deuterium ions and 1.8 MeV protons were used, respectively. The interstitial and substitutional nitrogen atoms as a function of

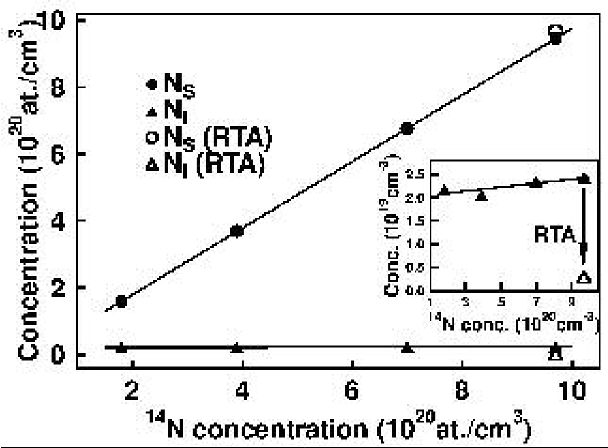

Figure 2. Interstitial and substitutional N concentrations as a function of mean N concentration in the samples. Substitutional N (N_S) increases linearly, while the interstitial N (N_I) has almost the same concentration in the whole N concentration region. The inset shows dramatic decrease of N_I after RTA.

concentration in GaNAs were determined by the nuclear reaction analysis utilizing the reactions $^{14}N(d,p)^{15}N$ and $^{14}N(d,\alpha)^{12}C$ and using the ion channelling technique.

Figure 2 shows the atomic concentrations of substitutional and interstitial nitrogen. The figure shows that substitutional N increases linearly with total N content. Very interesting is that the interstitial nitrogen concentration increases very slowly and stays at about 2.2 x 10^{19} at./cm^3 at the whole region. In the inset we see that RTA at 750 ^{o}C decreases the concentration of interstitial nitrogen by a factor of about ten.

It has been shown in the literature that the optimum annealing temperature to achieve maximum photoluminescence intensity is about 750 - 800 ^{o}C. Present results show that the majority of N interstitials are removed during RTA. Hence, we suggest that the non-radiative centers are defects involving interstitial N.

2.7.2 Stopping power data for the characterization of the samples

Accurate stopping power values are required in preparation and modification of materials in semiconductor technologies. Large-band-gap compound semiconductor materials such as GaN have important applications in optoelectronics devices. Various ion beam analytical techniques are frequently used for the characterization of such materials. The depth scales in these techniques are directly defined by the stopping powers which are necessary also for deriving the concentration values. Proton stopping powers are of primary importance since they are the basis for scaling of stopping powers for heavier ions. No previous stopping power data exist in the literature for any ions in GaN. For InP no data for hydrogen at energies over 500 keV can be found in the literature.

The stopping cross sections of the III-V semiconductor materials GaN and InP for 0.3 - 2.5 MeV protons were studied by the Rutherford backscattering technique [16]. A commonly used model ZBL-85 predicts the data correctly at the high energy end of our energy interval, but overestimates the stopping values by 7 % and 4 % for GaN and InP, respectively, at the lower energies.

Measurements and theory were applied to extrapolate the cross sections of the He(p,p) reaction for 1 – 5 MeV protons [25]. Advantages for using this elemental pair for detecting each other is due to their ability to probe deeper compared to heavier ions.

2.7.3 Computer modelling of radiation effects in compound semiconductors

A central theme within the project was to carry out computer simulations of non-equilibrium processes such as growth and irradiation of GaAs and GaN. This requires good interatomic potentials for the materials in question. Already in the planning stage of this work, we found that although some potentials do exist for GaAs, they were inadequate to study non-equilibrium effects. Furthermore, no potentials existed for GaN. Hence we first had to develop interatomic potentials for compound semiconductors, to facilitate achieving the main goal of simulating irradiation effects in them.

Development of interatomic potentials for compound semiconductors

We first developed Tersoff-like interatomic potentials for InAs, GaAs, and AlAs, which gave a good description of elastic properties and cohesion in all the materials, but could not describe phase transitions such as melting.

We then proceeded to develop a GaAs potential which allows modelling a wide range of properties of GaAs compound structures, as well as the pure phases of gallium and arsenic, including non-equilibrium configurations. Potential terms were developed separately for Ga, As and GaAs. Reference data were taken from experiments if available or computed by self-consistent total energy calculations within the local density functional theory. A number of tests that cover a wide range of structural geometries including the metallic phases of gallium and arsenic, point defect properties, elastic moduli, surface properties, and melting behaviour, were performed in order to validate the accuracy and transferability of the potential model. Application of the model to molten GaAs demonstrated the formation of gas-like bubbles inside the melt containing As_4 and As_8 weakly bound to each other. This demonstrated the usefulness of the potential for non-equilibrium studies.

Using the same approach as in the GaAs potential development, we proceeded with formulating a potential for GaN. The Ga part was identical to the one developed for GaAs. The GaN and N parts were newly developed. As for GaAs, we achieved a potential which can describe a wide range of properties of the systems, including elasticity, defects, melting, and amorphization. We have also developed a variation of the potential which has explicit ionic interactions included for the Ga-N interaction, to test what role ionic interactions may play.

Studies of irradiation effects in GaAs and GaN

Using the first interatomic potentials for InAs, GaAs, and AlAs (see above), we examined the effects of strain on the outcome of ion irradiation at InAs/GaAs and AlAs/GaAs interfaces. Our results for collision cascades at strained semiconductor interfaces showed a strong asymmetry in the distribution of vacancies and impurities produced at the interface. The effect was explained as a strain-induced effect analogous to the classical Kirkendall effect. We further showed that although the chemical composition of compound semiconductors does not strongly affect the overall evolution of collision cascades, the composition may in some cases have a significant effect on the final distribution of defects.

Using the more advanced potentials for the Ga, As, and GaAs system, we examined how a combination of ion range calculations and molecular dynamics computer simulations can be used to predict the atomic-level damage structures produced by MeV ions. The results showed that the majority of damage produced in GaAs both by low-energy self-recoils and 6 MeV He ions is in clusters, and that a clear majority of the isolated defects are interstitials. This has implications for the behaviour of GaAs components when ion implantation is used to introduce dopants into the material.

Experimental studies have shown that the behaviour of GaN during ion irradiation is even more complex than that in more traditional semiconductor materials. For instance, the damage level seems to depend strongly on the mass of the irradiating ions (even after normalization with the nuclear deposited energy), which has been interpreted as a sign of dynamic in-cascade defect annealing similar to that in metals. Overall, it is much more difficult to damage GaN than other semiconductors such as GaAs.

With our newly developed potential for GaN, we have started to

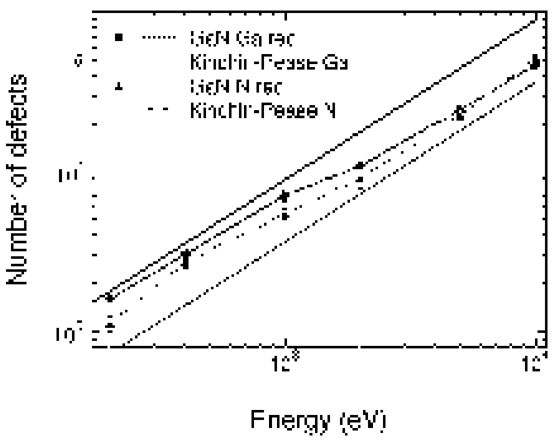

Figure 3. Damage in GaN obtained from molecular dynamics computer simulations, compared to the Kinchin-Pease predictions. The relatively good agreement, within a factor of 2, shows that cascades are roughly linear in GaN, and that there is no dramatic in-cascade annealing as in metals.

examine these questions. We have already been able to show that one major reason to the low damage levels in GaN is simply its mechanical hardness, which causes the threshold displacement energies to be higher, and hence damage level to be less than in other materials. This may not, however, be enough to explain fully the experimentally observed radiation hardness. We are currently examining whether e.g. the ionicity of the material could cause a dynamic in-cascade annealing effect proposed as an explanation to the experimental results. Without ionic effects, we have not found any signs of significant in-cascade annealing (Fig. 3).

2.8 Progress Report: Progress by VTT

We briefly summarise the main SIMS observations as follows.

Effects of oxygen on electrical and optical properties of Be and Si doped InP and GaInP were studied for MBE-grown samples, using SIMS, Van der Pauw Hall, deep level transient spectroscopy (DLTS) and the photoluminescence technique. We observed that the presence of oxygen drastically decreased carrier concentration and photoluminescence for these semiconductors. The nature of oxygen-related defects could be accounted for in a qualitative way. This work was done in collaboration with ORC and HUT 1.

Nitrogen concentration and lattice parameter in GaNAs were determined using SIMS and XRD techniques. A set of MBE-grown GaN_xAs_{1-x} ($0 < x < 3$ %) samples with a varying N content ([N]) was prepared. This work was carried out in collaboration with ORC and UH. A considerable negative deviation from Vegard's law was observed, as [N] exceeded 1.5 %, leading to an overestimation of [N] by up to 30 %, when deduced from XRD data. The complexity of GaNAs, already discussed elsewhere in this Consortium Report, was further reflected in our SIMS and XRD data on samples, which were prepared by Partner UH using ion implantation ([N] $\approx 2 \times 10^{16}$ cm^{-2}). These results showed that [N] measured with SIMS was *higher* than that obtained by XRD; the deviation from Vegard's law was positive. Other researchers have made similar observations.[32]

Many other material systems were studied by our SIMS method, including the determination of Zn concentration in InP, atomic diffusion of P in Ge, and impurity profiles in multi-layered GaInP / AlInP and GaAs / AlGaAs samples. This work was made in co-operation with ORC, UH, and HUT 1.

3 International Aspects

ORC The work at ORC was carried out in conjunction with international (and national) projects. Those relevant to MACOMIO were EU FALCON Network, EU ESPRIT SMILED, and EU COST-268. ORC also acted as a *Marie Curie Doctoral Training Site,* designated by the European Union for years 2000 - 2004, where foreign students participated in some of the workparts of this project.

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[32] Spruytte *et al.*¸ J. Appl. Phys. **89**, 4401 (2001)

There were 25 foreign research visitors (participating in MACOMIO) in 1999 – 2002 (and 15 other foreign researchers now at ORC). ORC's researchers made a number of short visits to laboratories and companies abroad and attended international conferences where they presented their latest results. We estimate that we co-operated with about 30 university groups and companies throughout the world during this project, and a considerable amount of this work was relevant to MACOMIO.

HUT 1 HUT 1 has the following main international collaborators in the field GaN and related materials: UNIPRESS, Polish Academy of Sciences, Poland (prof. T. Suski), Wright State University, USA (Dr. D. C. Look), Lincoln Laboratories, MIT, USA (Dr. R. Molnar), University of Warsaw, Poland (Prof. J. Baranowski), Naval Research Laboratories, USA (Dr. A. Wickenden and Dr. J. Freitas), University of Iceland (Prof. H. Gislason), Cornell University, USA (Prof. W. Schaff), West Virginia University, USA (Prof. T. Myers), Polytechnic University, Madrid, Spain (Prof. E. Calleja), Lawrence Berkeley National Laboratories (Dr. Z. Liliental-Weber).

HUT 2 International aspects regarding COMP / HUT 2 may be summarized as follows:

(i) Dr. Young Joo Lee from KAIST, Korea has participated full time in this project during 1998-2002. He continues to work at COMP on related projects.

(ii) Dr. Torsten Staab from Germany has been a EU-funded Marie Curie Fellow during 1998-2001, participating in the project. He has now moved to a faculty position at University of Bonn.

(iii) Dr. Chris Latham (University of Exeter, UK) has visited COMP for six months during 2000-2001, participating in the work on nitride materials.

(iv) Dr. Giuseppe Zollo (University of Rome, Italy) has visited COMP for six months during 2001, participating in the work on GaAs-based materials.

We have hosted several short-term visitors for scientific discussions concerning this project, including Dr. Chris van de Walle (Xerox Palo Alto, USA), Prof. S. Pantelides (Vanderbilt University, USA), Dr. Kurt Schröder (KFA Julich, Germany), Prof. Jim Greer (NMRC, Cork, Ireland), Prof. Luciano Colombo (University of Cagliari, Italy), Prof. Weimin Chen (University of Linköping, Sweden), Dr. Andrej Kuznetsov (University of Oslo, Norway) and Prof. Thomas Frauenheim (University of Paderborn, Germany).

COMP is a partner in several EU-funded European collaborations. Those relevant for this work include the ψ_k Network, the COST P3 Activity, and STRUC Programme supported by the European Science Foundation. COMP also participates in the Nordic network NOCDAD, supported by the the NorFA foundation (post-graduate research training).

UH The UH group has significant collaborations with 33 university laboratories, 7 research institutes, and 2 private companies. The work in this project has been performed in this network and the publications reported include the international collaboration. Working visits have been a part of the collaboration.

4 Publications and Academic Degrees

Table. Publications and academic degrees produced in MACOMIO. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs, topical review articles, and plenary or invited talks in international conferences in Section 6.3, and PhD and MSC Thesis in Section 6.4.

Partner	Type of publication	1999	2000	2001	2002	Total	Publication numbers
TUT1	Ref. journal art.	4	10	18	15	**47**	TUT1: 1-47
	Ref. conf. papers	7	14	40	13	**74**	TUT1: 48-121
	Monographs, Review articles, Plenary Talks	2	3	2	2	**9**	TUT1: 122-131
	Doctoral dissert.	2	-	1	2*	**5**	TUT1: 132-136
	Master degrees	2	7	1	3*	**13**	TUT1: 137-146, not all specified
TUT2	Ref. journal art.	-	1	1	2	**4**	TUT2: 1-4
	Doctoral dissert.	-	-	-	1	**1**	TUT2: 5
	Master degrees	-	-	1	-	**1**	TUT2: 6
HUT1	Ref. journal art.	12	5	10	7	**34**	HUT1: 1-34
	Monographs, Review articles, Plenary Talks	1	2	2	2	**7**	HUT1: 38-44
	Doctoral dissert.			1	2*	**3**	HUT1: 45-47
	Master degrees		2	1	3	**6**	HUT1: 48-53
HUT2	Ref. journal art.	4	3	5	7	**19**	HUT2: 1-19
	Ref. conf. papers	2	1	4	4	**11**	Not specified
	Monographs, Review articles, Plenary Talks	5	4	4	2	**15**	HUT2: 21-24, not all specified
	Doctoral dissert.	1	1	2	-	**4**	HUT2: 25-28
	Licentiate degrees	-	-	-	1	**1**	Not specified
	Master degrees	1	1	1	1	**4**	Not specified
UH	Ref. journal art.	5	10	8	6	**29**	UH: 1-29
	Ref. conf. papers	-	1	3	1	**5**	UH: 33-37
	Doctoral dissert.	-	1	1	-	**2**	UH: 38-39

	Master degrees	1	1	2	-	**4**	UH: 40-43
VTT	Ref. journal art.	5	3	2	2	**14**	VTT: 1-14
	Ref. conf. papers	-	1	2	-	**3**	VTT: 15-19

5 Other Activities

ORC MACOMIO has played a seminal role in basic research of compound semiconductors and optoelectronic devices and paved the way for the technology transfer to industry. It has helped to create steadily increasing industrial contacts regardless of today's global economic recession in ICT industry. ORC is presently co-operating with 18 companies worldwide.
The results of MACOMIO, in part, have encouraged us to set up a new company (Modulight Ltd., 2000), the second spin-off from our group. The two companies, Coherent-Tutcore and Modulight, now represent a new industry in Finland.

Patent applications:

- T. Leinonen, M. Pessa, S. Orsila, P. Uusimaa, Menetelmä optoelektronisen kvanttikaivokomponentin valmistamiseksi ja optoelektroninen kvanttikaivokomponentti, Patenttihakemus (patent application) PCT/FI01/00043, sisäänjättöpäivä 19.1.2001, etuoikeus: 21.01.2000, Suomi, 20000125
- M. Dumitrescu, M. Pessa, M. Saarinen, N. Xiang, Suuren hyötysuhteen omaava puolijohde-valolähde ja menetelmä sen valmistamiseksi, Patenttihakemus (patent application) numero 20010878, Tampereen Patenttitoimisto viitenumero TP100351 TPu/TS, 27.4.2001
- O.G. Okhotnikov, M. Guina, Modulator, Patent application, Patenttitoimisto Compatent Oy, applicants ref. nr. NC19588, agency´s ref. nr. P00420FI, 26.4.2002
- O.G. Okhotnikov, M. Guina, Method for organizing a mode-locked pulse train by pump modulator, Patent application, appl. number 20020467, Tampereen Patenttitoimisto ref.: nr. TP101238 TPu/EIP, 13 March 2002

Summer Schools, Symposia, Workshops:

- Organised Graduate School Course (GETA) on "Basic Topics on Fibre Optic Communications", Tampere University of Technology, Tampere, Sept. 25-29, 2000. Organisers: Prof. Oleg Okhotnikov and MSc Mircea Guina, ORC
- Organised International Summer School on "Advanced Topics on Fibre Optic Communications", Tampere University of Technology, Tampere, August 20-24, 2001. Organisers: Prof. Oleg Okhotnikov and MSc Mircea Guina, ORC
- Organised International Symposium on ”Current Trends in Semiconductor Physics and Optoelectronic Technologies”, Tampere University of Technology, Tampere, Nov. 16-17, 2001. Chairman: Prof. Markus Pessa, ORC; Proceedings Eds: Prof. Rolf Hernberg, Dept of Phys. of TUT, and Mrs Anne Viherkoski, ORC
- MACOMIO Workshop 1: May 12, 2000, ORC, Tampere

- MACOMIO Workshop 2: March 12, 2001, ORC, Tampere
- MACOMIO Workshop 3: March 6, 2002, ORC, Tampere

COMP We are collaborating with semiconductor manufacturers (Okmetic Ltd. in particular) to gain a better understanding and control of the crystal growth and processing of semiconductor materials relevant to micro- and optoelectronics. We have given popular presentation of our work in several occasions, both in national radio and TV and during the biannual Finnish Science Days, aimed at the general public.

6 Publications

6.1 Refereed Journal Articles

ORC

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[3] P. Savolainen;M. Toivonen;S. Orsila;M. Saarinen;P. Melanen;V. Vilokkinen;M. Dumitrescu;T. Panarello;M. Pessa, AlGaInAs/InP Strained-Layer Quantum Well Lasers at 1.3μm grown by Solid Source Molecular Beam Epitaxy**,** J. of Electronic Materials 28, pp. 980-985 (1999)

[4] S. Orsila;J. Köngäs;M. Toivonen;P. Savolainen;M. Jalonen;M. Pessa, Solid source molecular beam epitaxy growth and characterization of resonant cavity light-emitting diodes**,** J. Cryst. Growth 201/202, pp. 985-989 (1999)

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MATERIALS-BASED MICROWAVE FILTER TECHNOLOGIES

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Abstract

Filter technologies are crucial in modern telecommunications because of the various standards that apply to the different frequency bands. Microwave devices utilise the unique properties of piezoelectric and superconducting materials. Advanced materials physics is thus involved in the development of commercial filter components. The filter technologies and materials physics investigated in this project involve: (i) surface acoustic waves (SAW) and SAW components, (ii) bulk acoustic waves (BAW) and BAW devices, and (iii) high-temperature superconductors (HTS) and HTS filters. All these technologies also have important sensor applications. (i) SAW devices are expected to play an increasingly important role in electronic and signal-processing systems. We study surface acoustic waves both theoretically and experimentally. Theoretical modelling software has been developed for SAW material characterisation and the design of SAW filters. We are also engaged in prototype fabrication of high-frequency (for the 5–10 GHz range) SAW components, laser-interferometric characterisation of RF SAW components, and in a search for novel crystal cuts and materials (such as langasite) for RF applications. (ii) BAW devices: Challenges for the fabrication of BAW resonators include the control of materials properties and the crystal orientation. The ability to simulate these effects on the resonator characteristics is of utmost practical importance. In the Materials Physics Laboratory, we have been developing such simulation tools for resonator modelling. Other research topics in this area include simulating the propagation of acoustic wavefronts in anisotropic crystals and the study of diffractionless X-like bulk acoustic and optical waves and pulses in free space and in crystalline materials; recently, we have also become involved with the design and fabrication of radio-wave holograms. (iii) HTS devices: Research on the applications of high-temperature superconducting materials to microwave devices and systems. Commercial applications of HTS superconductivity are emerging, in particular for passive microwave devices. Superconducting microwave filters, antennas and systems are also being developed, and it is expected that superconducting electronic devices will grow in importance in the future. In this project, we have conducted research on the interaction between microwaves and superconductors, and microwave devices, particularly HTS bolometers and filters, on thin YBCO films have been fabricated and processed into devices.

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1 Partners and Funding

1.1 Materials Physics Laboratory, Helsinki University of Technology

The research group consists of professor Martti Salomaa, visiting professors Victor P. Plessky and Ali R. Baghai-Wadji, postgraduate students Mikko Kalo, Jouni Knuuttila, Julius Koskela, Saku Lehtonen, Tapani Makkonen, Johanna Meltaus, Janne Salo, Mikko Tuohiniemi, and Juha Vartiainen and the students Antti Holappa, Olli Holmgren and Kimmo Kokkonen. In addition, the IAESTE exchange students Matthias Weber (Germany) and Joanna Olzewska (Switzerland) have participated in the research.

1.2 Funding

Table 1. Funding of the project in 1000 FIM during 1999-2002. The internal funding by HUT consists of manpower costs and operational expenditures. The funding provided by the Academy of Finland is the EMMA project "Materials-Based Microwave Filter Technologies" reported here. The private Foundations include the NOKIA Foundation, the Finnish Cultural Foundation, the Magnus Ehrnrooth Foundation and the Foundation for the Promotion of Technology (Finland).

Partner	Funding Organisation	1999	2000	2001	2002	**Total**
HUT	HUT	160	160	160	160	**640**
	Academy (EMMA)	180	320	320	180	**1000**
	Private Foundations	100	100	100	100	**400**
	Industry (Foreign Resources)	600	600	600	600	**2400**
Total		**1040**	**1180**	**1180**	**1040**	**4440**

2 Research Work

2.1 Objectives and Work Plan

Surface Acoustic Waves (SAW) and SAW devices.

Theoretical modeling of SAW filters; design of SAW components, in particular high-frequency (from the 2.4 Bluetooth band to 5 – 10 GHz, including the WLAN band) SAW filters; laser-interferometric analysis of SAW filters.

Bulk Acoustic Waves (BAW) and BAW devices.

Simulation tools for resonator modeling; modeling the propagation of acoustic wavefronts in anisotropic crystals; the study of diffractionless X-like bulk acoustic and optical waves and pulses in free space and anisotropic crystalline materials. – Change/extension of the work plan: Recently, we have in addition become involved with radio-wave hologram design and fabrication, also to produce propagation-invariant radio waves, in collaboratorion with the Radio Laboratory at Helsinki University of Technology.

High-Temperature Superconductors (HTS) and HTS components.

Research on the application of high-temperature superconducting materials to microwave systems has been pursued, in particular passive components including microwave filters, antennas and bolometers. Technologies for HTS thin-film processing have been developed for component fabrication.

2.2 Progress Report: Research Results

Surface Acoustic Waves and SAW devices.

Comprehensive theoretical and modeling tools have been developed (papers [1], [9], [11], [12], [21]) and recently applied in SAW tag development (papers [25], [26]).

Novel acoustic loss mechanisms occurring in high-frequency SAW devices have been experimentally discovered (papers [2], [6], [13], [18]) and explained theoretically (papers [6], [20]) – this work has also led to patents.

An optical laser interferometer for SAW device modeling has been developed (paper [8]).

High-frequency SAW devices have been designed and fabricated with the help of nanolithography, in collaboration with the Department of Physics at the University of Joensuu, Finland (paper [3]) and Nanocomp Ltd (Joensuu).

Bulk Acoustic Waves (BAW) and BAW devices.

Extensive work on BAW simulation software development has been carried out (paper [14]), the simulation tool for resonator modeling has been applied to the determination of the wave dispersion relations from our laser-interferometric measurements (paper [27]).

Diffractionless acoustic and optical waves have been classified and their theory has been extended to anisotropic materials and to arbitrary speeds, including subsonic nondiffracting waves (papers [4], [10], [15], [16], [24]).

Radio-wave holograms have been designed and fabricated to produce and measure propagation-invariant radio waves in free space and radio-wave vortices (papers [17], [22], [23]) in collaboratorion with the Radio Laboratory at HUT.

High-Temperature Superconductors (HTS) and HTS components.

A laser-ablation facility has been developed (paper [7]) for HTS thin-film fabrication. The thin films are used for HTS device fabrication, including superconducting filters and bolometers. Processes for HTS component fabrication have been developed.

Industrial implications.

Patents on avoiding acoustic loss mechanisms in SAW devices; application of leaky longitudinal SAW modes in commercial Bluetooth-band filters; patents on the piston mode in BAW resonators; analysis of commercial SAW filters for industrial R & D.

3 International Aspects

International visibility of the work performed:

Several refereed contributions to international conferences, including invited talks (publications [28 - 56]) at the MTT-S International Microwave Symposia (Los Angeles, 1999; Seattle, 2002), the IEEE Ultrasonics Symposia (Lake Tahoe, 1999; San Juan, Puerto Rico, 2000; Atlanta, 2001; Munich 2002), International Symposium on Acoustic Wave Devices for Future Mobile Communication Systems (Chiba University, Japan, 2001), the European Time and Frequency Forum (Neuchâtel, Switzerland, 2001), the Symposium “Physics and Engineering of Millimeter and SubMillimeter Waves“ (Kharkov, 2001), the European Optical Society Topical Meeting on Electromagnetic Optics (Paris, 2001), the International Conference on Terahertz Electronics (Charlottesville, 2001), the IEEE International Conference on Infrared and Millimeter Waves (San Diego, 2002).

International collaborators include Dr. V. P. Plessky (Switzerland, France), Managing Director C. S. Hartmann (USA), Prof. A. T. Friberg (Sweden), Prof. A. R. Baghai-Wadji (Austria), Dr. S. Kondratiev (Switzerland), Dr. T. Thorvaldsson (Switzerland), and Dr. S. V. Biryukov (Russia); several visitors, including Professors Jun-ichi Kushibiki (Department of Electrical Engineering, Tohoku University. Senadai, Japan) and Seth Putterman (Department of Physics, UCLA, Los Angeles, USA); Participation in the EUREKA project E! 2442 SUMO: “New Surface Acoustic Wave Filter Generation for Mobile Telecommunications“ (France and Finland). Main industrial partner: Thales Microsonics (TMX), Sophia-Antipolis, France.

Martti Salomaa Visiting Professor at the Technical University at Vienna (Gastprofessor fűr das Fach Materialwissenschaften am Institut fűr Industrielle Elektronik und Materialwissenschaften) in 2001 (a series of 16 lectures on: “Applied Superconductivity“) and again in 2002 (a series of of 15 lectures on: “Advanced Materials: Theory and Applications“).

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1999	2000	2001	2002	**Total**	Publication numbers
HUT	Ref. Journal Papers	7	5	8	7	**27**	1–7, 8–12, 13–20, 21–27
	Ref. Conf. Papers	8	3	10	7	**28**	28–35, 36–38, 39–48, 49–56
	Monographs	-	-	-	1	**1**	57
	Doctoral dissert.	1	-	1	-	**2**	58–59
	Licentiate degrees	-	1	1	2	**4**	60–63
	Master degrees	1	3	2	-	**6**	64–69

5 Other Activities

Lecture series arranged at Helsinki University of Technology:
- “Applied Superconductivity“ (professor Martti M. Salomaa)
- “Surface Acoustic Wave Physics and Devices for Mobile Communication“ (visiting professor Victor P. Plessky)
- “Wavelet Theory I and II“ (visiting professor A. R. Baghai-Wadji)
- “Photonic Crystals“ (visiting professor A. R. Baghai-Wadji)
- “SAW Sensors“, Research Seminar in Materials Physics (visiting professor Victor P. Plessky and professor Martti M. Salomaa)

National Award for the Master’s Thesis of the Year, May 2001:
- Johanna Meltaus: “Design, Fabrication and Measurement of a High-Temperature Superconducting Bandpass Filter“ (Tekniikan Akateemisten Liitto TEK ry, the Prize was shared with MSc Mikko Valkama, Tampere University of Technology)
- Johanna Meltaus also won the first prize for the best Master’s Thesis in the Department of Engineering Physics and Mathematics at Helsinki University of Technology in December 2001.

6 Publications

6.1 Refereed Journal Articles

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6.3 Monographs

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7 Other References

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[71] BAW devices: **http://focus.hut.fi/projects/saw/saw_fbar.html**

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[73] HTS and laser ablation: **http://www.hut.fi/Units/AES/projects/prlaser/pld.htm**

CHARACTERIZATION OF DEFECTS IN NOVEL SILICON-BASED MATERIALS SYSTEMS

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Abstract

A consortium of five laboratories is formed in order to characterize defects in silicon material system. Two partners are silicon processing laboratories; the others specialize in advanced characterization methods such as Raman and positron (PAS) spectroscopy and transmission electron microscopy (TEM). First class of defects to be characterized consists of recombination centers in IC, epitaxial, and SOI wafers, and structural defects in MEMS wafers. These defects are studied by lifetime measurements utilizing also PAS and TEM methods. Detection of iron and copper contamination is successfully done using lifetime methods. TEM and PAS turn out to be powerful in studying defects in SOI and SmartCut wafers.

Light emitting centers in silicon-silicon dioxide system form the second class of defects studied. Samples are grown using molecular beam deposition (MBD), ion implantation and low pressure chemical vapor deposition (LPCVD), followed by various annealing procedures. The samples are thoroughly characterized utilizing the full arsenal of the methods available at the partner laboratories. A coherent picture of the light emission mechanism has been created: the emission originates from oxygen related defects occurring at the interfacial region between the nanoscale silicon and silicon dioxide. Light emitting device (LED) demonstrations have been fabricated covering the visible spectral range from red to blue. Emission intensity is rather low, but external quantum efficiencies as high as $2 \cdot 10^{-3}$ have been reached. A strong spectral narrowing of emission is found in some LEDs at higher current levels similar to that occurring in injection lasers. Optical gain in nanosecond time scale is observed using optical pumping. These findings hint to the possibility to realize in the future a silicon based laser.

1 Partners and Funding

1.1 Electron Physics Laboratory, Helsinki University of Technology (EPL/HUT)

The research group consists of subproject leader professor J. Sinkkonen, senior researchers PhD S. Novikov and A. Malinin, postgraduate students H. Väinölä, J. Storgårds, M. Yli-Koski, M. Palokangas, A. Haarahiltunen, O. Kilpelä and students H. Holmberg, T. Toivola and T. Saloniemi.

The funding of the EMMA project provides salaries for two postgraduate students. The other members of the group are funded by Helsinki University of Technology, by the postgraduate schools of Academy of Finland, and other projects by Tekes.

1.2 Laboratory of Physics, Helsinki University of Technology (LP/HUT)

The research group consists of subproject leader professor K. Saarinen, senior researchers PhD J. Dekker and J. Slotte, postgraduate students J. Oila, V. Ranki, A. Laakso, and J. Nissilä and students R. Aavikko, A. Pelli, and S. Hautakangas.

The funding of the EMMA project provides salaries for one postgraduate student. The other members of the group are funded by Helsinki University of Technology, the postgraduate schools by Academy of Finland, and projects from the Academy of Finland.

1.3 Laboratory of Physical Chemistry, University of Helsinki (LPC/UH)

The research group consists of a subproject leader professor M. Räsänen and a senior researcher Doc. L. Khriachtchev. The funding of the EMMA project was used for the salary of a senior researcher.

1.4 Laboratory of Electronics and Information Technology / Microelectronics Laboratory, University of Turku (LEIT/UT)

The research group consists of subproject leader doctor R. Punkkinen, senior researcher Phil.Lic. L. Heikkilä, postgraduate student H.P. Hedman and students M. Hirvonen, M. Meretoja and T. Rumpunen.

The funding of the EMMA project provided salaries for two postgraduate students. The other members of the group are funded by the University of Turku and by TEKES.

1.5 Centre for Electron Microscopy, Tampere University of Technology (CEM/TUT)

The research group consists of subproject leader professor T. Lepistö and researcher S. Karirinne.

1.6 Funding

Table 1. Funding of the project in 1000 FIM in 1999-2002. Internal funding consists of manpower costs and operational expenditures provided by the organization. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organization	1999	2000	2001	2002	**Total**
ELP/HUT	HUT	450	900	600	300	**2250**
	EMMA/Academy	300	600	600	200	**1700**
	Grad. Schools/Academy	150	150	300	225	**825**
	Tekes	100	470	720	240	**1530**
	Industry	30	60	85	65	**240**
LP/HUT	HUT	70	210	210	110	**600**
	EMMA/Academy	70	210	210	110	**600**
LPC/UH	EMMA/Academy	70	210	210	110	**600**
LEIT/UT	UT	160	480	480	240	**1360**
	EMMA/Academy	135	470	470	125	**1200**
	Tekes	280	630	-	-	**910**
CEM/TUT	EMMA/Academy	70	210	210	110	**600**
Total		**1885**	**4600**	**4095**	**1835**	**12415**

2 Research Work

2.1 Objectives and Work Plan

Defect characterization is a very broad field. Therefore the subject was in the ordinary research plan limited so as to fit with the needs of the Finnish semiconductor industry, strengthen the ongoing research activities, and also include novel trends in silicon materials research. As the result, the focus was directed to:

(1) Recombination centers in epitaxial and SOI wafers

Recombination centers are important from the industrial point of view because they are correlated with the quality of the wafer production and the subsequent device processing. Typically the density of the recombination centers is well below 10^{13} cm^{-3}, i.e. below the sensitivity limit of most analytical methods. DLTS (Deep Level Transient Spectroscopy) and recombination lifetime measurements are two well known exceptions, being sensitive enough. Lifetime measurement is a fast, non-contact, non-destructive method which suits well with the industrial environment. On the other hand, DLTS requires Schottky devices to be processed. It is therefore more time-consuming and destructive in nature, but offers more detailed information on a particular recombination center.

In this project, the emphasis was put on the interpretation of the lifetime measurements in (a) high quality, homogeneous IC wafers and especially in (b) epitaxial and SOI wafers, where the semiconductor to be characterized occurs as a thin layer. The lifetime studies are supported by DLTS and other electrical measurements.

(2) Structural defects in MEMS wafers

Structural defects (point defects, dislocations, voids, etc) occur in all kinds of wafers. They influence the mechanical as well as etching properties of wafers, being especially important in MEMS applications. In this project, structural defects are characterized by a variety of methods available in the partner laboratories.

(3) Defects associated with light emission

The origin of the light emission from samples containing nanostructured silicon was not known at the time the project plan was made. There were several competing mechanisms. Quantum confinement model anticipates that the emission takes place in nanoscale silicon crystallites. Other models involve interface states or impurity states to explain the light emission. Now the emission is better understood, but still a decisive, quantitative and generally accepted model is missing.

In this project the light emission problem was attacked with the full strength of the consortium. The general aim was to (a) gain understanding of the light emission mechanism, (b) enhance the emission efficiency by various processing means, and (c) tailor the emission spectrum by utilizing microcavities.

The consortium was formed in such a way that it is capable of sample growth, processing and characterization. Most of the samples were made inside the consortium, the epitaxial silicon and SOI wafers being the only exception. The roles of the various partners in the consortium were as follows:

Electron Physics Laboratory specializes in semiconductor technology. Being a member of the Microelectronics Center of HUT, it has access to a complete silicon processing facility. In addition, it has an advanced MBD (Molecular Beam Deposition) system which is utilized in this project to make the light emitting samples. Also relevant to this project are the characterization facilities, i.e. the lifetime scanner (μPCD, SPV, Kelvin probe), the DLTS equipment, and a variety of optical and electrical measurement systems. The laboratory was responsible for the lifetime studies, DLTS measurements, and fabrication and characterization of light emitting samples.

The experimental group of the Laboratory of Physics has studied defects in semiconductors by positron spectroscopy since 1985. Internationally, the group has played an important role in the development of positron techniques and their applications to defects in semiconductors. The role of the Laboratory of Physics in the Consortium is to utilize PAS to (1) characterize the Si/SiO_2 and Si/SiO_N samples and thus obtain experimental information on the atomic structures responsible for the light emission, and (2) characterize the vacancy defects in epitaxial and SOI wafers.

The Laboratory of Physical Chemistry specializes in solid-state optical spectroscopy and photochemistry. It has facilities for the full range of optical spectroscopy methods that are UV-VIS-IR absorption, Raman scattering and time-resolved photoluminescence measurements. The laboratory was responsible for studies of structural and emission properties of the Si-based materials.

The Laboratory of Electronics and Information Technology (Microelectronics laboratory from beginning of year 2002) specializes in semiconductor technology. We have constructed a CVD (chemical vapor deposition) multichamber processor, having epitaxial layer growth, plasma etcher, and sputtering possibilities. We have also improved old 100 mm optical lithography equipment to 150 mm wafers (down to 2 μm line width) that can be used to manufacture various structures, e.g. thin film Si/SiO_2 nanostructures. The laboratory has the following characterization capabilities: CV measurements, optical spectroscopy (0.2 μm - 1.8 μm) for electroluminescent samples, and ellipsometry.

The role of the laboratory is to fabricate various nanoscale structures, e.g. very thin Si/SiO_2 superlattices, to measure the electroluminescence spectra of the light emitting superlattice samples in the visible (300 – 800 nm) and in the IR (900 – 1700 nm) regions, to characterize the electrical properties of the superlattice structures, and to design novel component structures based on light emitting samples. Internationally, our group has been a pioneer by detecting in 1999 the narrowing of the EL spectra of a four layer pair Si/SiO_2-superlattice, when the driving current was increased [18]. This has later inspired the measurements of light amplification in SiO_2 layers containing silicon nanoparticles.

The Centre for Electron Microscopy is focused on electron microscopical studies and microstructure characterization of materials. The research activities include both basic as well as applied materials research. In CEM, detailed cross-sectional analytical transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) analyses are undertaken to study the structure of the light-emitting Si/SiO_2 multilayers and the microstructural defects in SOI and MEMS wafers.

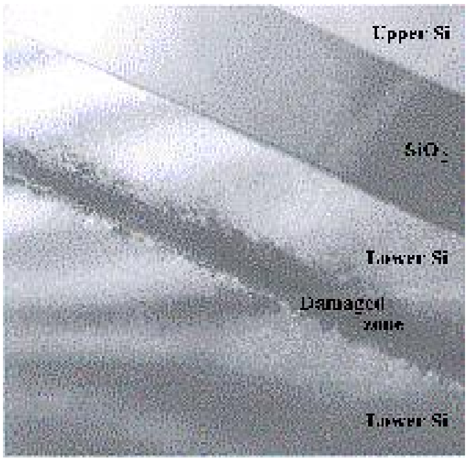
2.2 Progress Report: Common Themes

(1) Recombination centers in epitaxial and SOI wafers

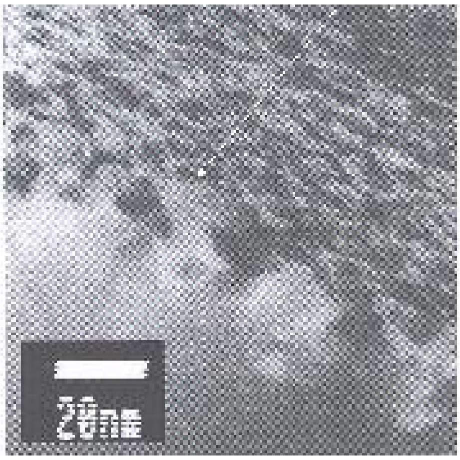
In order to interpret the lifetime measurements of epitaxial and SOI wafers, an analytical two-layer model was developed. The model was verified by accurate numerical simulations (Silvaco). The bonding interface in the SOI wafers studied was situated in the oxide layer. It turned out that the carrier lifetime was rather insensitive to the defects in the bonding interface. On the other hand, the performed C-V measurements revealed charge trapping at interfaces depending on the bonding temperature. The interface defects were also studied by PAS. For more details see sections 2.3, 2.4 and 2.6.

(2) Structural defects in MEMS wafers

Transmission electron microscopy turned out to be a powerful tool in the study of structural defects. Incomplete bonding was seen in some SOI wafers. Occasionally a double layer was formed at the bonding interface. Fig. 1 shows the formation of cracks in hydrogen implanted SmartCut wafers. For more details see section 2.7.



a)



b)

Fig.1. Cracks in <111> direction in SmartCut wafers. In 1a, the interface of bonded wafers is shown, with SiO_2 thermally grown on the upper wafer, and with H_2^+ ion implantation damage inflicted on the lower wafer, before bonding. An enlarged view of the damaged zone in 1b reveals the series of parallel cracks.

(3) Defects associated with light emission

A large number of samples grown by different methods were made as shown in fig.2.

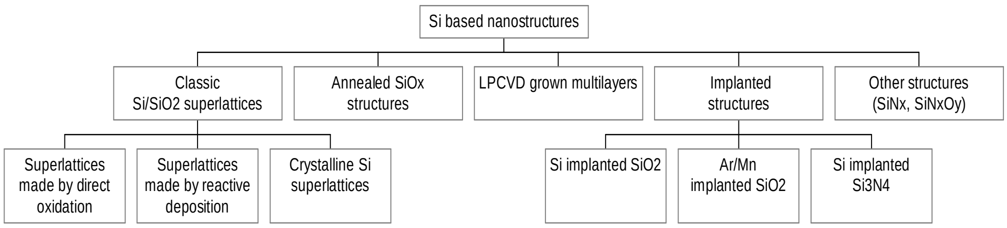


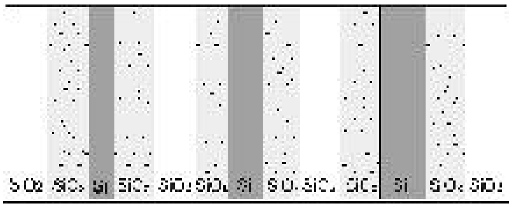
Fig. 2. Types of samples grown in the project.

After various annealing procedures, the samples were subjected to Raman, PAS and TEM studies. Also, complementary optical and electrical measurements were done. The outcome of these studies can be summarized as follows:

a) Mechanism of light emission in Si/SiO_2 systems

All samples contained nanostructured silicon, i.e. layers in superlattices or nanoscale particles in SiO_2 matrix. The emission spectrum shows a much weaker dependence on the dimension of the structure than predicted by the quantum confinement model. The evolution of the ordered phase of the nanostructured silicon can be seen in Raman spectra, but correlation between the Raman and photoluminescence spectra is missing. Growth conditions of oxide greatly influence the emission intensity. Thus, the light emission most likely originates from the interface region existing between silicon and perfect SiO_2 as shown in fig. 3a. For further details see section 2.5.

a)



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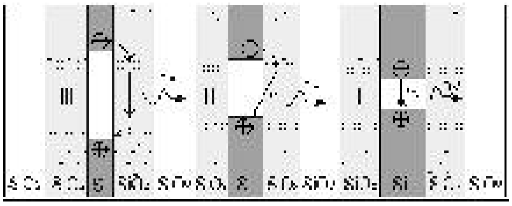


c)

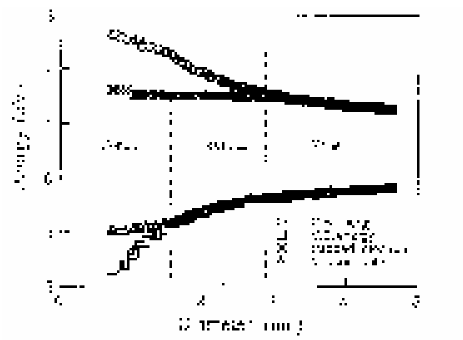


Fig. 3. Nanoscale silicon – active SiO_x interface region – perfect SiO_2 structure (a), energy band diagram (b), and the model of Wolkin et al. [49] for radiative transitions (c).

The energy band diagram of this complex is depicted in fig. 3b. The active light emitting centers are presumably oxygen-associated defects in the interface region. According to the calculations of Wolkin et al. [49], the radiative transitions take place as follows (see fig. 3c): If the nanoparticle size is large (>3 nm), the optical transition is over the band gap of the nanoscale silicon (region I in fig. 3c). Owing to quantum confinement, the band gap of the nanoparticle increases with decreasing size. Below 3 nm, the upper state is the interface defect state (region II in fig. 3c), and finally below 1.6 nm, also the final state of the transition is the defect state (region III). Region III corresponds to the blue spectral range whereas region II covers the yellow-red range. The mechanism shown in fig.3 is consistent with our findings in light emission. It is also gaining acceptance among the other research groups.

b) Emission spectrum

The electroluminescent devices are mostly of the MOS-diode type (fig. 4). The active SiO_2 layer thickness is typically 100-300 nm. The upper transparent electrode is usually a thin metal layer (20 nm Au, Cr) or ITO layer. Electroluminescence is excited by hot electron impact collisions. LED demonstrations covering the visible spectral range from red to blue were made. The best external quantum efficiency values obtained were $2 \cdot 10^{-3}$.

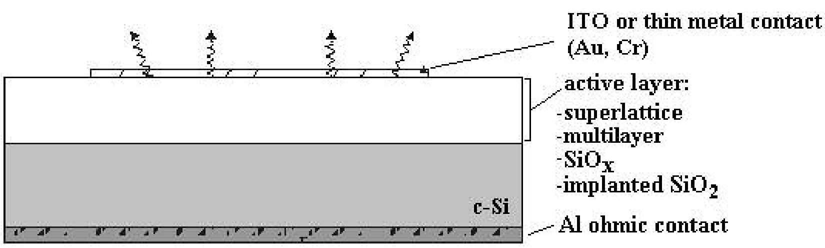
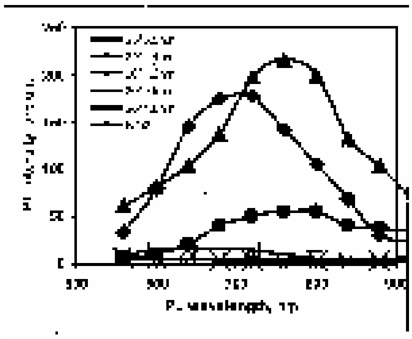


Fig. 4. Structure of MOS type silicon LED.

Typical PL and EL spectra are shown in fig. 5. Excitation of PL is made by 488 nm Ar laser. Absorption of the exciting light takes place at silicon nanocrystals, where electron-hole pairs are created. The excited electrons are then very rapidly transferred to the upper levels of the radiative transitions explained in the previous section, whereafter they recombine. For more details see sections 2.3, 2.5 and 2.6.

a)



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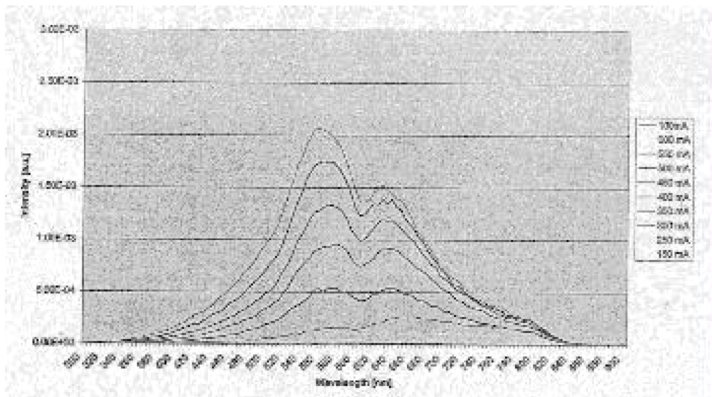


Fig. 5. PL spectrum of Si/SiO_2 superlattices with varying Si layer thickness excited by 488 nm Ar laser (a) and EL spectra of a LPCVD grown Si-LED at various currents (b). The decrease of intensity in (b) at around 620 nm is of instrumental origin.

c) Light amplification

From the scientific point of view, the most significant results of the project are the laser-type narrowing of EL spectrum under high excitation current (see section 2.6) [18] and optically pumped light amplification (see section 2.5) [10]. Light amplification was measured in the planar waveguiding mode (fig. 6) in nanosecond time scale. The time constant of PL decay is typically a few microseconds. The finding of optical gain in the nanosecond regime is very important because it shows that silicon based optoelectronics can be fast enough for telecommunication applications.

The first paper on optical gain in silicon based material systems, by Pavesi et al. [49], appeared in 2000. Reference [10] which reports the gain result of the recent project is the third published paper on the subject. The result of fast optical gain has been later verified also by the group of Pavesi both experimentally and theoretically. A four-level model [47] was successively used to study the dynamics of PL.

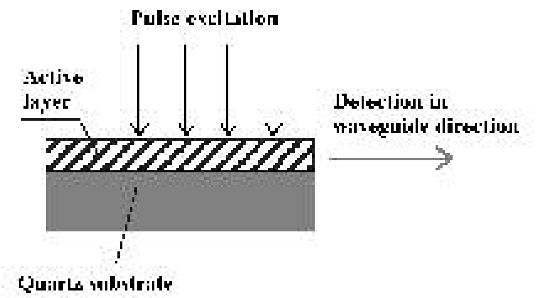


Fig. 6. Experimental arrangement used in the light amplification study.

2.3 Progress Report: Progress by the Electron Physics Laboratory

(1) Recombination centers

In recombination studies, the goal was to develop methods based on lifetime measurements which would be utilized to characterize the quality of silicon materials, especially epitaxial and SOI wafers. In these cases, the semiconductor to be studied is a thin layer, which introduces problems both in measurements and in their interpretation.

The research included modeling and simulation of the measurement methods themselves and development of improved theoretical tools of interpretation. Simulation of the μPCD method (microwave photoconductance decay) was done by calculating the microwave reflectance from the photoexcited wafer [1?]. It was shown that the reflectance method introduces a weighting function to the local photoconductivity. The weight function turns out to be proportional to the intensity of the incoming microwave radiation. By tailoring the antenna configuration, this offers the means to enhance the sensitivity and selectivity of the μPCD method. The properties of the epi-antenna, which is a special design for epitaxial wafers, are well understood from the basis of simulations. Furthermore, new measurement options such as the use of bias light and temperature dependent lifetime measurements were developed. Using bias light, it is possible to tune the dominating SHR recombination term from low to high injection regime, and obtain more information on the physical parameters of the recombination centers. Similarly, the trap state energy and capture cross sections of electrons and holes can be extracted from temperature dependent lifetime measurements [25]. The success of the T dependent μPCD was, however, limited owing to hardware problems in the temperature controlling unit.

An exact three-dimensional analytical model of photoconductance transient was developed for homogeneous wafers [31]. This is needed in the case of high quality IC wafers, where the surface recombination easily dominates in the measured lifetime. The 3D model was utilized to check the validity of the more frequently used one-dimensional models. For epitaxial wafers, a 1D-two-layer model for lifetime measurements was developed [6]. The model includes the effect of the internal potential barrier between the epitaxial layer and substrate. This is an important improvement compared with the existing published models. Analytical models were verified by a numerical simulator (Silvaco). As an example, fig. 7 shows the time dependent photocarrier distribution in a p/p^+ epitaxial wafer.

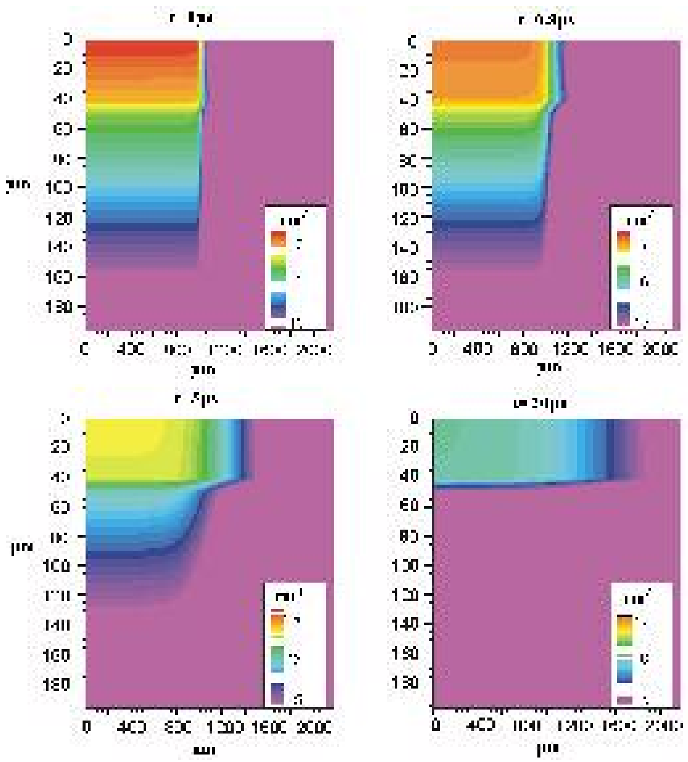


Fig. 7. Minority carrier density in an epitaxial p/p^+ system (p^+ substrate) at different times after the photoexcitation.

The experimental work was largely concentrated on the determination of metal contamination in wafers. Emphasis was put on iron and very recently on copper impurities [25]. Iron contamination can be quantitatively extracted from SPV (surface photovoltage) measurements.

t=0 t=0.8 µs t=5 µs t=20 µs

(2) Defects associated with light emission

a. Microcavity LEDs

The emission spectrum can be tuned by utilizing microcavities. For optical studies, planar structures where the active layer is placed between two Bragg mirrors are easily made. A lateral LED with microcavity is shown in fig. 8. The structure was grown by MBD. The active layer is conducting Sb-doped SiO_x ($x \sim 10^{-2}$) of thickness λ, and the mirrors are $\lambda/4$ layers of undoped Si and SiO_2.

µm

µm µm µm µm

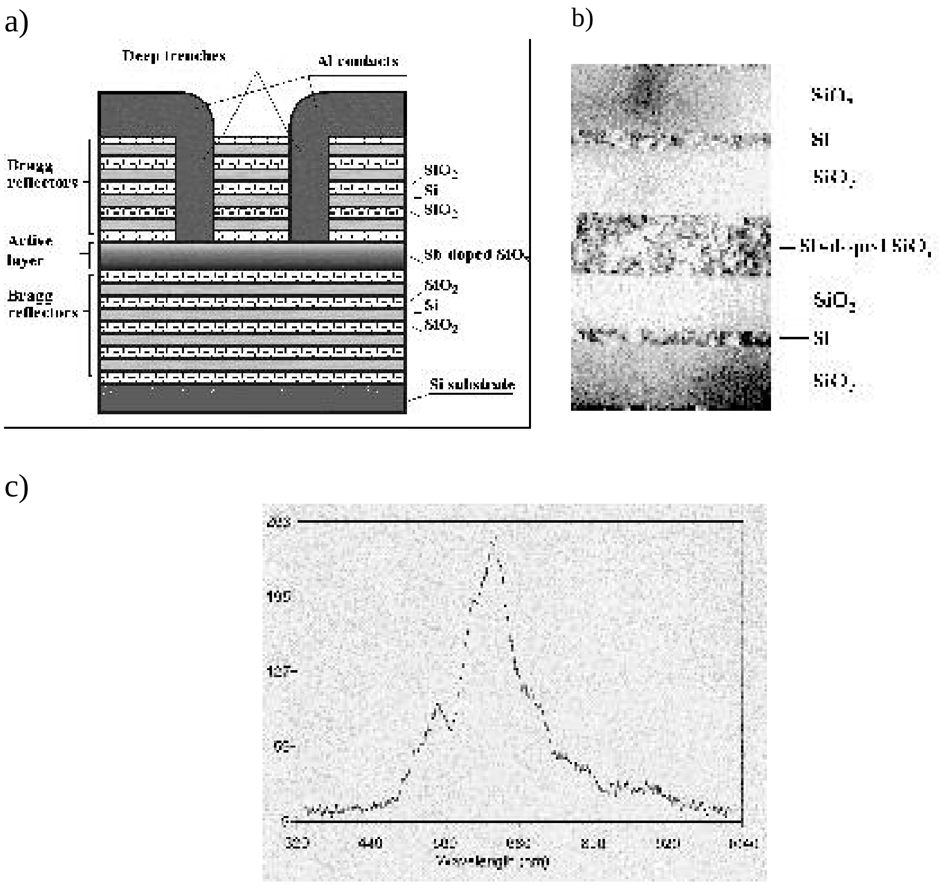


Fig. 8. Lateral microcavity LED. A schematic (a) and a TEM picture (b) of the microcavity, with an active layer and Bragg reflectors comprised of four SiO_2/Si layer pairs, and EL spectrum (c).

EL is excited by the lateral current flowing in the active layer. The separation of the current contacts was 5 μm. The effect of the microcavity is seen as the narrowing of the spectrum. The width of the spectrum in fig. 8 is about 100 nm or roughly 0.1 eV, which is considerably less than the original width of 0.3 - 0.5 eV.

b. Mn doped SiO_2

The mechanism of light emission in silicon rich silicon dioxide was largely understood by the model explained in section 2.2. The model involved oxygen related defect states. Unfortunately, no experimental data exist yet on the detailed atomic scale structure on these defects. Manganese is a well known yellow light emitting center utilized for example in commercial ZnS displays.

In this project, an experiment was made to compare the emission properties of Mn and the blue centers in Si implanted SiO_2. Manganese was introduced into SiO_2 by knock-on implantation. The EL spectrum of the silicon-implanted sample containing manganese is shown in fig. 9 [34]. In addition to the blue peak, the spectrum has also a Mn-related yellow peak. Mn density is 10^{20} cm^{-3} as obtained from SIMS analysis.

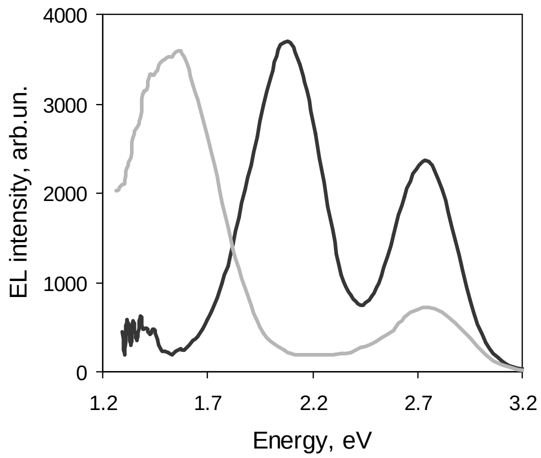


Fig. 9. EL spectrum of a Si-implanted, Mn-knock-on-implanted sample (dark line) vs. sample without Mn (light line).

c. Crystalline Si/SiO superlattices

Epitaxial deposition of alternating thin silicon and oxide layers by the molecular beam deposition (MBD) method allows the growth of low-dimensional silicon with greater precision and dimensional control than e.g. the annealing of SiO_x into SiO_2 and nc-Si [50]. Successive cycles of silicon deposition at high temperature and exposure to gaseous oxygen at room temperature can be used to fabricate nanoscale periodic structures. Multilayer samples of varying deposition parameters were grown using this method in order to validate the process for epitaxial deposition. Fig. 10 shows a typical early sample with just two oxide monolayers. Eventually, up to 20 layer pairs per sample were successfully created.

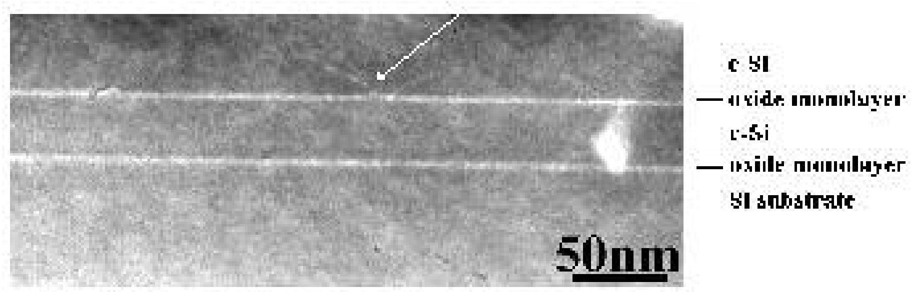


Fig. 10. TEM image of crystalline silicon with two oxide monolayers. Some line defects visible on the upper interface (arrow). Later superlattice samples had 4 nm c-Si layers between oxide monolayers.

The crystalline quality of the top Si layer was evaluated using Hall and conductance measurements and RHEED and TEM imagery. The results indicated monocrystalline or nearly monocrystalline growth of silicon atop oxide monolayers. Devices fabricated by this method have potential both in light emission and general SOI applications. Crystalline Si/SiO superlattice might act as a high band gap semiconductor lattice matched to silicon, making possible silicon based heterojunction device technology.

2.4 Progress Report: Progress by the Laboratory of Physics

Positron spectroscopy has been applied to study defects and interfaces in superlattices of silicon and silicon dioxide grown on silicon substrates. Superlattices were grown by molecular beam deposition and plasma enhanced chemical vapor deposition. Positron measurements show that in the superlattices of hydrogen grown layers, positron annihilation is composed of annihilation in the amorphous silicon and annihilation in the oxide, with minimal contribution from the interfaces. If the superlattice is free of hydrogen, strong positron trapping at the interfaces is observed. Similarly, positron trapping is detected for interfaces between the oxide matrix and Si nanoparticles, formed either by implantation or annealing of superlattices.

Comparisons between oxide/Si and oxide/SiC interfaces show that the defects acting as positron traps are on the oxide side of the interface. Furthermore, the annihilation characteristics of positrons trapped at interfaces show that annihilations occur predominantly with the oxygen valence electrons. The atomic structure of the defects can thus be associated with an open volume defects, surrounded by oxygen atoms. For example, Si vacancies in the oxide near the interface, similar to non-bridging oxygen or peroxyl defects, may be negatively charged and act as positron trapping sites.

The studies of semiconductor-on-insulator (SOI) systems have been initiated together with Okmetic Ltd. We studied wafers bonded at different temperatures, leading to different strengths of the bonded interface. Both thermal bonding and Ar and O plasma activated bonding was studied. Positron experiments show that the defect densities at the bonded interface change dramatically with the bonding temperatures. Furthermore, we found that oxide/oxide plasma activated bonding created more defects than similar Si/oxide bonding.

2.5 Progress Report: Progress by the Laboratory of Physical Chemistry

(1) Raman scattering of ultra-thin amorphous Si layers.

We studied thoroughly Raman scattering of very thin (≤ 3.5 nm) Si layers constituting Si/SiO_2 superlattices (SL) and grown by molecular beam deposition [17]. It was shown that the Raman spectra exhibited a systematic dependence on thickness of the Si layers, which highlighted the variety of disordered microstructures in the Si/SiO_2 superlattices. A clear change in the vibrational properties was found to occur in the 0.8 to 3.5-nm thickness region, roughly around 2 nm. In particular, the Raman spectra are typical for amorphous silicon for the thicker layers, and the characteristic phonon band practically disappears for the thinner layers, presumably representing another form of Si coordination with a small Raman scattering cross-section. In agreement with this observation, absorption of the material changes essentially with Si-layer thickness as in more details described later. Photoluminescence (PL) is detected from the Si/SiO_2 SLs, the samples with 1.2-nm and 1.8-nm Si layers being the most efficient emitters, and the PL is somewhat blue-shifted with the decrease of Si-layer thickness. The Raman spectra of the as-deposited Si layers show no sign of nanocrystalline structure at any Si layer thickness so that the observed photoluminescence cannot be connected with Si nanocrystallites. Annealing strongly changes the Raman and photoluminescence spectra, a well-ordered Si phase appears in the material, but its increase does not correlate with the photoluminescence, which further disregards it as an emitter. Nevertheless, the emitting phase was not identified in the Raman spectra.

(2) Optical model of an as-deposited Si/SiO_2 SL

Raman scattering and PL measurements can be influenced by the optical properties of the system. A quantitative model of a Si/SiO_2 SL was developed and practically applied to Raman scattering and PL measurements [13]. Interference-induced modification of Raman scattering and PL was quantitatively studied for Si/SiO_2 SLs on Si and Al substrates, and the developed optical model described well all observed features. By analysing the experimental reflection spectra of Si/SiO_2 SLs on Si and Al substrates, we obtained optical parameters of amorphous Si layers with thickness below 4 nm. Both refractive index and extinction coefficient were found to decrease with Si-layer thickness, and this behaviour is proposed to reflect interaction of the Si network and the oxide surrounding. In accordance with the Raman spectroscopic results described earlier, the essential change of the optical properties occurs for amorphous Si layers about 2 nm thick. From these optical measurements, we concluded the decisive role of Si/SiO_2 interface in establishing the optical properties of a SL. It was estimated that the 0.7-nm thick SiO layer could roughly approximate the Si/SiO_2 interface in an as-deposited SL. For better description, a smooth distribution of optical properties in SL bulk should be considered.

(3) Laser annealing as a fingerprint of a molecule-like emitter

PL spectra of as-deposited Si/SiO_2 SLs were found to change under Ar^+-laser irradiation, and this effect of laser annealing becomes stronger for thinner amorphous Si layers [13]. For 1-nm-thick Si layers, a prolonged laser exposure decreases the PL intensity at 550 nm by a factor of 10 and red shifts its maximum by about 50 nm, which indicates reorganisation of the emitting phase under laser irradiation. Importantly, the Raman spectra do not change upon laser annealing, confirming its invisibility by Raman spectroscopy, which establishes doubts about photon quantum confinement in amorphous Si layers. It should be emphasised that “laser annealing” does not mean any temperature effect but rather applies to a photochemical (local) reorganisation of the emitting centres. As discussed later, the emission probably originates from Si=O covalent bonds stabilised at the Si/SiO_2 interface, and laser annealing might mean their reorganisation into a bridged Si-O-Si structure with a different (higher) excitation energy.

(4) Thermal annealing (RTA): Effect of substrate material

The Si/SiO_2 superlattices on fused quartz and crystalline Si substrates were annealed up to 1200 °C (RTA method) [7]. For the SLs on Si substrates, the annealing was found to lead to unstressed crystallisation, and visible PL (~2.1 eV) strongly increases with the annealing temperature for samples with thinner Si layers (≤2.5 nm). The annealed SLs on quartz substrates exhibit a higher disorder, tensile stress and weaker visible PL. The comparison between Raman and PL spectra does not support assignment of the annealing-enhanced visible photoluminescence to quantum confinement in Si crystallites. These results highlight the connection between lattice disorder and PL. Stresses seem to contribute essentially to crystallisation process. Laser-induced decrease (laser annealing) of PL after this "intermediate" annealing is observed, supporting photochemical reorganisation of the network.

(5) Thermal annealing of Si/SiO_2 materials (furnace)

It is valuable to compare the annealing effects on two conventional types of Si/SiO_2 materials, Si/SiO_2 SL and Si-rich silica (SiO_x) films, both prepared with a molecular beam deposition method. The as-grown material is amorphous, and disordered Si inclusions are seen in Raman spectra for samples with higher Si contents [13]. Annealing at 1150 °C in nitrogen atmosphere leads to ordering of Si grains, and the typical crystalline size is estimated to be 3-4 nm as judged by the Raman spectra [17]. For all samples, an annealing-induced increase of PL at ~ 1.6 eV is observed, and its resulting position is quite independent of the initial sample architecture. Furthermore, this PL is practically identical for CW and pulsed excitation at 488 nm as well as for pulsed excitation at various wavelengths (266 - 488 nm), and the order of PL lifetimes is 1-10 μs [L. Khriachtchev and S. Novikov, unpublished]. No correlation between the crystallite concentration and the PL intensity for the annealed samples was found, and the strongest PL was obtained for two samples with less defined crystallisation. The effect of laser irradiation on PL of annealed samples is small, meaning that furnace annealing produces deeper stabilisation minima on the potential surface for the emitting centres.

(6) Fast optical gain

It is known that the emission of nano-Si has a lifetime in microsecond region, which limits its applicability in optical communication. In order to get fast emission from Si crystallites, one can use a laser approach involving stimulated emission promoted by population inversion. We found experimental evidence of population inversion and amplified spontaneous emission of Si nanocrystallites embedded in a SiO_2 surrounding under pumping with 5 ns light pulses at 380, 400, and 500 nm [10]. The material was prepared with thermal annealing (1150 °C) of a SiO_x film, which produces crystallites with diameters of about 3 nm. As an important property, our experiments showed a short lifetime of the population inversion, allowing the generation of short (a few ns) amplified light pulses in the Si/SiO_2 lattice. The estimate for optical gain in the present samples is 6 cm^{-1} at 720 nm. This very short lifetime of the amplified spontaneous emission is extremely important for applications.

(7) Emitting phase and gaining scheme

Based on the lack of correlation between Raman and PL spectra of Si/SiO_2 material, one can conclude that the direct emission from Si grains (quantum confinement model) is improbable. A better candidate is some molecule-like emitter (interface defect), for example, involving =Si=O (silanone) fragment. Several structures with different transition energies have been found computationally [51],[52]. In particular, this image is supported by the independence of PL on the excitation wavelength. The gaining phase should be generally similar, although the net gain might be perturbed by the spectral dependence of the oscillator strengths. Our experiments on fast gain were performed in a wave guiding geometry where the film with a relatively high refractive index worked as an optical fiber. The optical absorption at the wavelength of amplification is very small, making a three-level amplification system absolutely impossible here. The observed optical gain must originate from a more complicated process, say, involving a classical four-level scheme. For instance, the four-level scheme can be controlled by Si=O bond distance in the ground and excited states of a silanone-containing emitter.

(8) Red PL of gold island films

Electroluminescence measurements are often performed through semitransparent gold films, and the result can be influenced by self-emission of the gold layer. That is why we comparatively studied PL and morphology of gold films prepared with a sputtering method [8]. The ultra-thin films (≤10 nm) efficiently emit light above 600 nm, which differs dramatically from the known emission of thick gold films. The absorption mechanism in ultra-thin gold films is presumably contributed to by their island structure, promoting interacting plasmons. The collective plasmon states of island films decay radiatively, producing the extraordinary red emission observed under excitation at 488.0, 514.5 and 632.8 nm. The red photoluminescence of ultra-thin films is substrate-dependent and correlates with the surface morphology analyzed by using atomic force microscopy and resistance measurements.

(9) Structural studies of Si-C films

Si-C material is another possible candidate for optoelectronic applications. The key questions are whether Si crystallizes in amorphous carbon and whether PL from Si grains can be found there. We studied Si-C films (Si content from 0 to 33 at. %) prepared with a pulsed arc discharge method [9,15]. The structural modifications were introduced by annealing up to 1100 °C, by irradiation with 53-MeV $^{127}I^{10+}$ ions, and by deposition onto heated substrates, and then characterized by Raman spectroscopy. For all the treatments, the structural modifications decreased when the Si concentration increased. Moreover, for high Si content (33 at. %), the energetic iodine ions are found to recover efficiently the structure degraded in preliminary high-temperature annealing. The experiments demonstrate Si-induced stabilization of the three-dimensional Si-C network, which is interpreted as deepening the corresponding potential energy well. It is highly possible that Si-C films can possess a superior thermodynamic stability for an optimal Si concentration. Si diffusion coefficients in amorphous carbon were measured. However, we detected neither Si grains nor noticeable PL.

2.6 Progress Report: Progress by the Laboratory of Electronics and Information Technology / Microelectronics Laboratory

(1) Electrical characterization of SOI wafers

Electrical properties of Silicon-On-Insulator wafers were characterized. The samples manufactured by Okmetic Ltd. were similar to those investigated by positron annihilation spectroscopy at the Laboratory of Physics (see 2.4). Bonding was carried out either thermally or by plasma activation with low temperature anneal. Oxide/oxide or silicon/oxide bonding was used in such a way that each of the samples had 100 nm thick oxide layer between the two bonded wafers. One of the wafers was then totally removed by grinding and etching, resulting in the simple structure of p-type silicon wafer with 100 nm of silicon dioxide on the top and the original bonding interface at different depths of the oxide layer.

Metal-Oxide-Silicon structure was used for the measurements. In order to minimize the need of further processing of the samples, the metal contacts were made at room temperature by Au-sputtering through a mechanical mask. The method was qualified by using samples where the contacts were made both by traditional photolithography and by simple Au sputtering. In comparing the results, the sample preparation method was found to be suitable for the measurements that do not require heating of the sample.

High frequency capacitance-voltage measurements were used to determine the total oxide charge density. It was found out that the charge density was strongly dependent on the anneal temperature. It was also found that the silicon/oxide bonding resulted into an unstable and negatively charged oxide. No significant difference was found between Ar and O plasma activated samples.

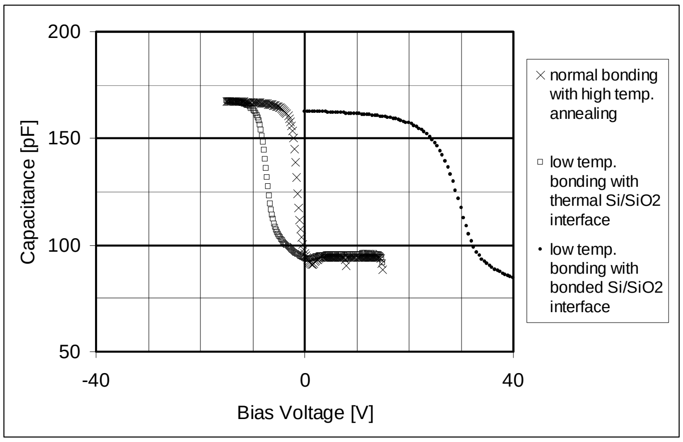


Fig. 11. Typical high frequency C-V curves for different samples showing the effect of the bonding process to the total oxide charge density.

The so-called conductance method was used to investigate the density of Si/SiO_2 interface traps in the samples. This is a variable frequency method where the parallel conductance of the MOS capacitor structure is in focus. The conductance, representing the loss mechanism due to interface trap capture and emission of carriers, is a measure of the interface trap density.

Much higher interface state densities were found on plasma activated samples compared to the high temperature annealed ones. On the other hand, no considerable difference was found between the samples having the original bonding interface in the middle of the oxide layer and the silicon/oxide bonded samples having the bonding interface at the Si/SiO_2 interface of the final test structure. This means that even in this latter case, the defects related to the bonding interface were not in electrical communication with the underlying silicon layer.

The insight into the quality of the oxide layer revealed by electrical measurements was partly different from the picture achieved by the positron annihilation spectroscopy at the Laboratory of Physics. This is partly because the electrical method was sensitive only for the states at the Si/SiO_2 interface. Also the different behavior of donor and acceptor type states in these measurements was considered, but the type of the interface states could not be concluded from the electrical data for these samples.

Other measurements included current-voltage measurements where the breakdown voltage of the oxide layer was investigated. Critical field of the order of 10 MV/cm was found for all of the samples.

(2) Light emission in crystalline Si/SiO_2 layer structures

This part of the project concentrates in investigation of electroluminescence (EL) in silicon nanostructures on silicon wafer surface and in surface layers made by CVD process, widely used in IC industry. Experimental results have given the knowledge that typically the EL spectrum is broad [Sec. 2.2 fig. 4b] and usually has a peak wavelength in red or in IR region. In spite of a large number of experimental tests with different Si layer thicknesses, the spectrum is still broad and does not obey the quantum confinement model strictly, as mentioned in 2.2. However, in some cases, a laser-type narrowing of EL spectrum has been found. These samples have a structure similar to the one shown in Sec. 2.2, fig. 5, and having four or more Si/SiO_2 layer pairs as the active layer. The top gold electrode is made by sputtering and the back contact is made from silver paste. EL peak narrowing happens "usually" when the driving current to the 5 mm^2 electrode rises over 500 mA. Simultaneously with the narrowing, the peak intensity rises to more than ten times the usual value for a wider spectrum [see fig.12].

In the samples where silver paste is used as a back contact and the superlattice layers are not doped, the current can flow in both directions and we can see a colour change [see fig. 13].

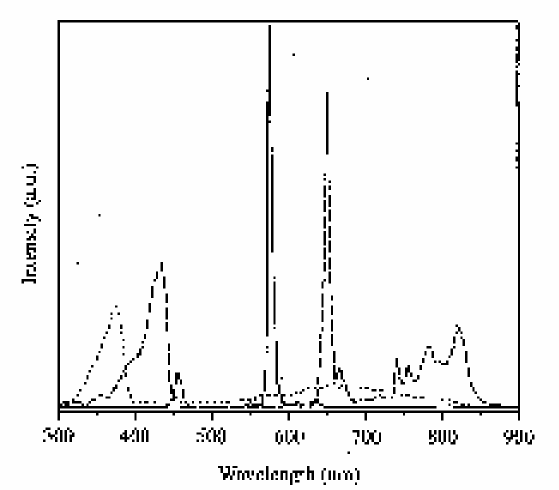
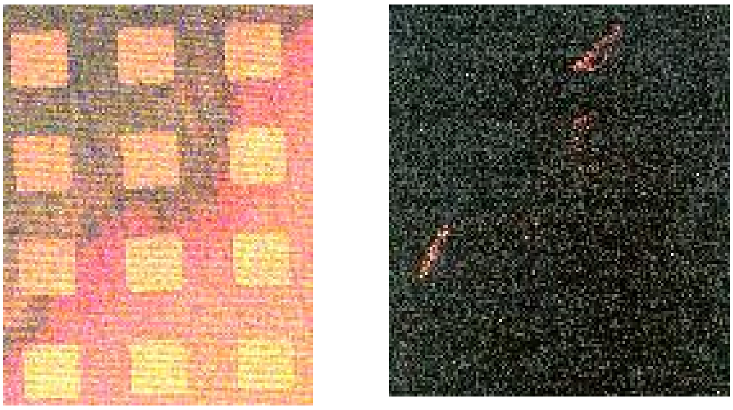


Fig. 12. Narrowing of EL spectrum of four layer pair Si/SiO_2 superlattice grown on an epitaxial silicon layer (solid line). A similar structure without epitaxial layer (dash line). The dotted line shows typical intensity for wide spectrum at smaller current densities around 650 nm.

Fig. 13. The change in color with driving voltage. EL is yellow when the top gold electrode has negative voltage compared to p-type silicon substrate and EL is red if top electrode has positive voltage.

If we look at EL samples by optical microscope, light typically originates from small dots whose diameter is measured to be less than 600 nm. The density of these dots varies depending of the layer structure in sample. In the case of a bare 7 nm thick thermal oxide layer on p-type silicon wafer, the EL dot density at 150 mA current is 490 mm^{-2}. In the case of CVD oxide layer, the dot density is around 2000 mm^{-2}; and if we have CVD oxide + thin poly silicon layer, the dot density is around 1300 mm^{-2}. It must be noted that these electroluminating dots meet at least one important criterion for light sources is Si IC technology: they are small!

In order to try to enhance the EL intensity from Si/SiO_x structures, the electric current is concentrated with lithography: small holes are opened to the first layer (thermal oxide) and the Si/SiO_x layers are then deposited (see fig. 14a). The recent results (see fig. 14b) show that luminescence can be found from the openings (squares 30 μm × 30 μm). This proves the spots can be manufactured to selected areas. The first experiments have shown that some luminescent spots can emit light with both polarities as in the case of bigger electrode areas.



a) b)

Fig. 14a. A photograph from a matrix of micrometer scale (square 30 μm × 30 μm) openings in thermal oxide where four layer pairs of Si/SiO_2 superlattice are grown by CVD. Lower right half of the picture is covered by semitransparent gold electrode. In 14b, dotted EL light is emitted through openings covered by gold electrode. Intensity of EL is higher near the border of the semitransparent top gold electrode. The color of EL in figure is not real because of poor imaging technique.

In the future, adding a waveguide to this LED structure makes transferring the light signal possible.

By integrating a resonator structure to these light sources, the light intensity can probably be enhanced together with spectral narrowing, and so these LEDs become more suitable for practical purposes. The most demanding task is to improve this LED with a resonator structure towards an electrically driven Si/SiO_2 laser.

2.7 Progress Report: Progress by the Centre of Electron Microscopy

The main area of research has been the structure characterization of photo- and electroluminescence emitting silicon structures and different SOI-structures. Structure characterization was done with two analytical transmission electron microscopes (Jeol JEM 2010 and Philips CM 200 FEG) in which parallel electron energy loss spectrometry (PEELS) and energy dispersive spectrometry (EDS) have been detached. With these microscopes, analysis near atomic resolution is also possible.

(1) Photoluminescence samples

Samples emitting photoluminescence were twenty period Si/SiO_2 superlattice structures grown at HUT by the molecular beam epitaxy (MBE) technique. From these samples, the effects of annealing, silicon layer thickness, and the substrate material to the light emitting silicon superlattice structure have been studied. The annealing was done either at 1200°C degrees for five seconds (rapid thermal annealing, RTA) or at 1000°C for one hour (furnace annealing, FA). The thickness of the silicon layer varied between 10 nm and 1.5 nm while the silicon dioxide layer was kept constant (1 nm).

Emission increased when silicon layer thickness decreased from 10 nm to 2.5 nm and the strongest emission was observed when the silicon layer thickness was ≤ 2.5 nm. As a result of annealing, the originally amorphous structure changes to nanocrystalline in all the samples studied (fig. 15).

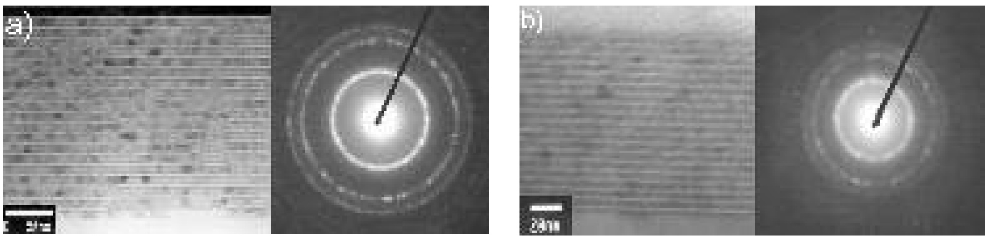


Figure 15. TEM micrographs and SADPs from a) 20 x 10 nm and b) 20 x 5 nm Si/SiO_2 superlattices after annealing.

When silicon layer thickness falls below a certain limit (2.5 nm), after annealing, no distinct silicon and silicon dioxide layers can be observed; the layers merge into uniform emission layer in which little silicon particles are in the amorphous matrix (fig. 16). No major differences between different annealing methods (RTA and FA) were observed.

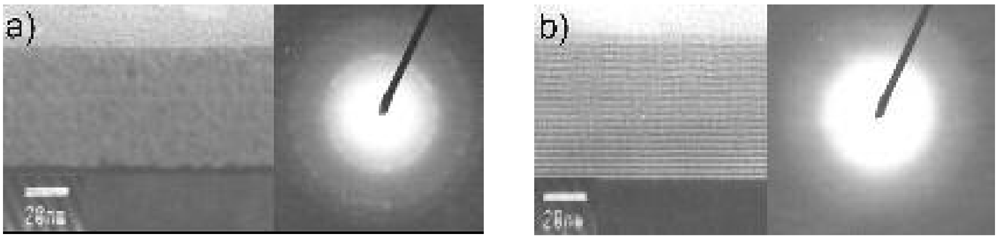


Figure 16. TEM micrographs and SADPs from 20 x 2 nm Si/SiO_2 superlattices grown on silicon a) after and b) before annealing.

The presence of nanocrystals was confirmed by HRTEM analysis (Fig. 17). This analysis clearly shows that after annealing, elliptical and spherelike nanocrystals appear in amorphous matrix.

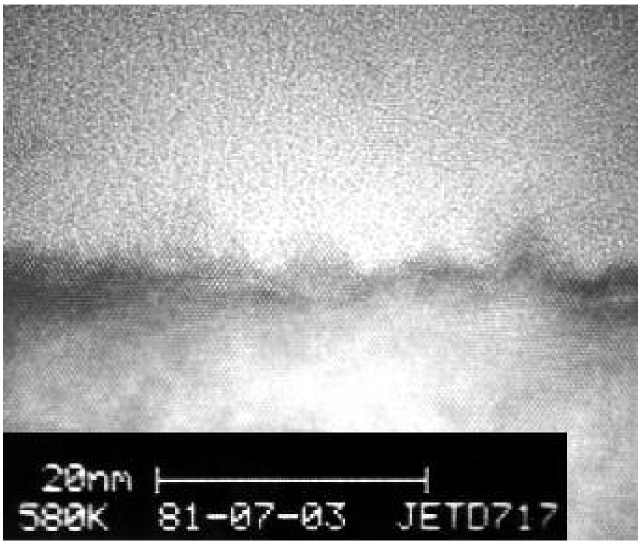


Figure 17. TEM micrograph of the 20 x 2nm superlattice after RTA annealing.

The merging of the silicon and silicon dioxide layers has been studied with samples where the thickness of the silicon dioxide layer has been increased into 2 nm and silicon layer thicknesses are 3, 2.5, and 2 nm, respectively. Annealing temperatures and times were the same. After annealing, silicon and silicon dioxide layers merged as before when the silicon layer thickness was ≤ 2.5 nm. When the layer thickness was increased above 2.5 nm, silicon and silicon dioxide layers remained separate (fig. 18). For all samples, structure changed from amorphous to nanocrystalline after annealing. According to these results, the layer merging is dependent on silicon layer thickness.

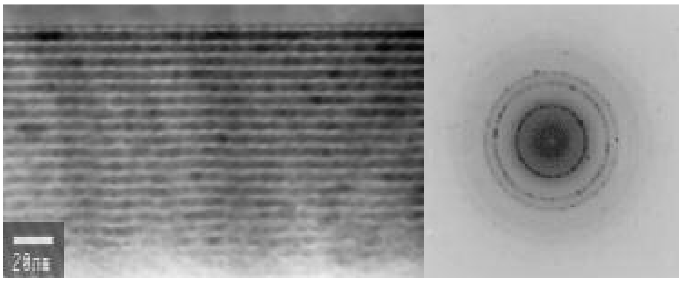


Figure 18. BF and SADP images of the 20 x 3 nm superlattice after annealing.

The effect of substrate material was studied with 20 x 5 nm and 20 x 2 nm samples grown onto silicon and quartz substrates. Results from samples grown on silicon are presented in figs 15 and 16. All samples were annealed with RTA method. Measured photoluminescence was stronger for samples grown onto silicon than samples grown onto quartz. From selected area diffraction pattern (SADP), no difference in crystallization between 20 x 5 nm samples was observed (Fig. 19).

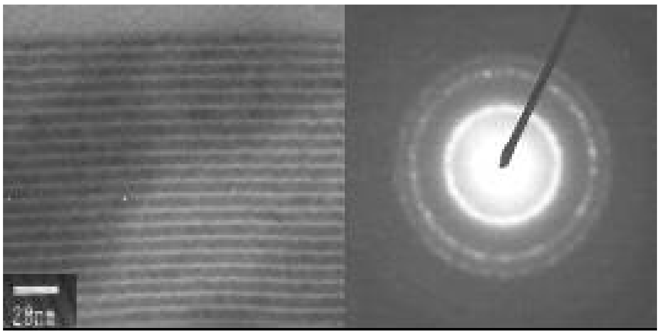


Figure 19. TEM bright field image and SADP of the 20 x 5nm Si/SiO_2 superlattices grown on fused quartz substrate after RTA annealing.

In the case of 20 x 2 nm samples, a difference in crystallization was detected so that a structure grown onto silicon substrate was more crystalline than a structure grown onto quartz substrate (figs. 19 and 20).

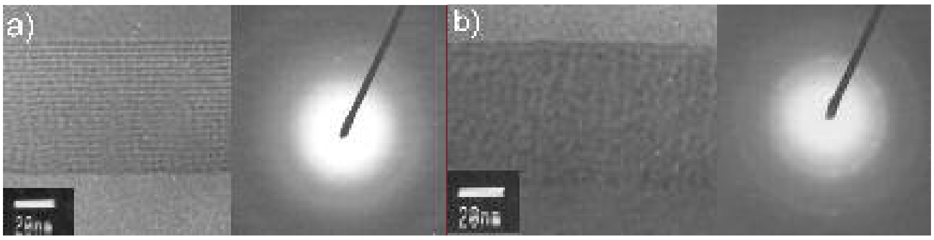


Figure 20. TEM bright field image and SADP of the 20 x 2 nm Si/SiO_2 superlattice grown on fused quartz a) before and b) after RTA treatment.

When the whole layer pack thickness of the 20 x 2 nm sample is measured from the picture of the unannealed (fig. 16b) and RTA annealed (fig. 16a) samples deposited onto silicon, it was observed that the thickness after annealing was ~20 % thinner than before annealing. The observed layer pack shrinking on silicon substrate could indicate that layers are more compact, to relax the built-in stress in the superlattice structure. Because of that, the level of crystallization and the number of possible defects operating as recombination centers for light emission may be somewhat higher. This could explain the more intense photoluminescence observed from these samples.

From the results, two articles have been written, of which 'Substrate dependent crystallization and enhancement of visible photoluminesence in thermal annealing of Si/SiO_2 superlattices' has been published in Applied Physics Letters [7]. The other article 'Substrate and annealing dependent crystallization of Si/SiO_2 superlattice structures' has been published in the Proceedings of the Royal Microscopical Society 12^{th} "Microscopy of Semiconducting Materials" Conference [28].

(2) Electroluminescence specimens

Samples emitting electroluminescence were Si/SiO_2 superlattice structures or CVD and thermal oxides, grown at TUT with chemical vapor deposition (CVD) method. From these samples, the effects of the oxide type and superlattice structure on light emission were studied. An Au layer was sputtered to the sample surface to form a contact. Samples were not annealed. Preliminary analysis showed that a CVD-oxide sample emitted light in both forward and reverse bias and that the wavelength of the emitted light changed from red to yellow with the bias direction. The CVD oxide structure showed signs of possible gold diffusion. In the case of thermal oxide, this was not observed. Moreover, in the case of superlattice and thermal oxide, emission is not as strong as for CVD-oxide, and emission is observed only at forward bias. From these results, a poster and an abstract were presented at the Scandem 2001 conference [30].

(3) Okmetic SOI samples

Two out of three samples were activated with Ar plasma treatment. The unactivated sample went through a heat treatment at 1100°C, whereas the activated samples were heated at 400°C and 100°C, respectively. In the case of the first two samples, the joint strength was strong, and in the case of the latter sample, it was weak.

The Ar plasma activation and temperature probably affect the joint strengthening. On the basis of the bright (BF) and dark field (DF) as well as g-vector analyses made, an extremely local ‘double layer’ structure forms at the thermal side of the structure. At the bonded side of the structure, precipitates are observed. These precipitates move away from the interface as the temperature is increased from 100°C to 400°C. In the sample without Ar activation, no precipitates were detected.

(4) SmartCut samples

SmartCut samples were prepared so that thermal oxide was grown onto one ordinary Si wafer and H_2^+ ions were implanted into another. After implantation, the wafers were bonded. The hydrogen ion implantation moves the lattice atoms, and hydrogen reacts with silicon, forming complexes and a damage layer. In this damage layer, hydrogen creates microcracks, which causes the wafers to cut off after heat treatment at the point of the hydrogen profile. Three samples were prepared. In these samples, hydrogen was implanted into wafers with different crystal orientations (<100>, <111> and <110>). The other wafer was always at <100> orientation. From the samples, the microcracks, their orientation and their number were studied.

When the orientation of the hydrogen implanted wafer was either <100> or <111>, the microcracks were clearly visible and their orientation followed the 111 direction (fig. 21).

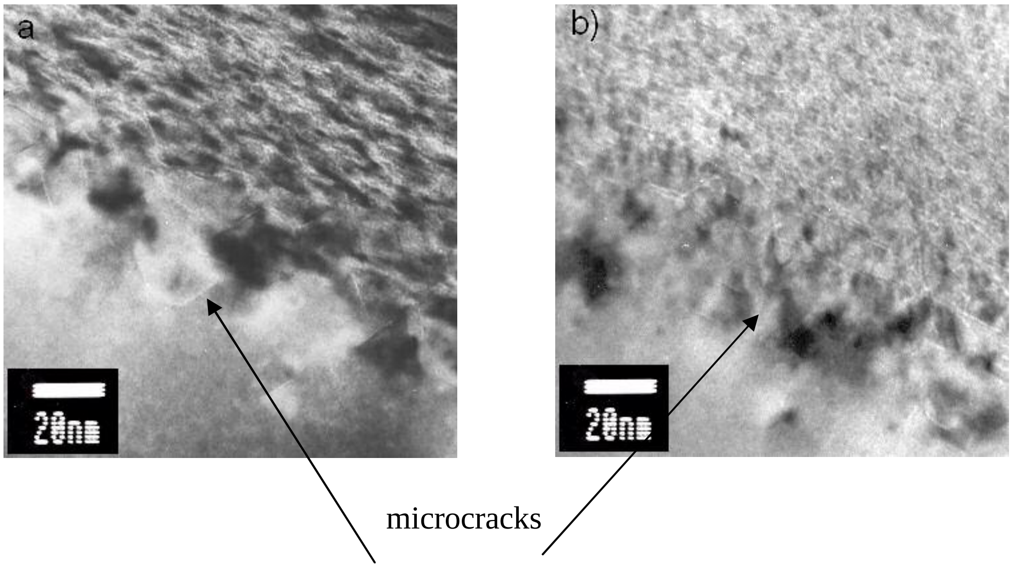


Figure 21. BF image from microcracks in the hydrogen damage layer with wafer orientation of a) <100> and b) <111>.

The exact number of the cracks is hard to calculate, but at estimation, more cracks appear at <111> orientation. When the orientation of the hydrogen implanted wafer was <110>, the cracks were difficult to see at the same two beam conditions as the previous samples. It seems that at this orientation, very few microcracks are formed.

3 International Aspects

Reference [10] which reports on the optical gain found in the present project is the third published paper on the subject, and the first one reporting its speed in the nanosecond regime. The result has been noticed by the scientific community. Dr Khriachtchev (LPC/UH) was invited to give a lecture at the NATO advanced research workshop “Towards the First Silicon Laser”, to be held on September 21-26, 2002 in Italy.

Prof. L. Pavesi, whose group published the first paper on optical gain, visited Finland and partner laboratories during May 29 – June 2, 2002. He gave two lectures on the subject in the Annual Seminar of the present project (Kallvik, May 30, 2002).

There has been constant cooperation with various laboratories of the A.F. Ioffe Institute (St. Petersburg, Russia) during the project.

The Laboratory of Physics in Helsinki Univ. of Technology has the following international collaborators in the field of Si related materials: University of Aarhus, Denmark (prof. A. Nylandsted Larsen), Bell Laboratories, Lucent Technologies, USA (Dr. P. Citrin), Royal Institute of Technology, Sweden (Dr. A. Kuznetsov), Chalmers University of Technology, Sweden (Prof. E. Sveinbjörnsson) and CNRS-Orleans, France (Dr. M.-F. Barthe).

The Centre for Electron Microscopy has extensive co-operation with University of Oxford (Dept. of Materials), Stockholm University (Dept. of Structural Chemistry), and Chalmers Technical University (Dept. of Experimental Physics). At the beginning of the year 2000, the Centre for Electron Microscopy paid a three-month visit to the University of Stockholm, Department of Structural Chemistry. During this time, the ten credit point course 'Structure analysis with diffraction and electron microscopy' was completed. In January 2002, S. Karirinne visited Göteborg at Chalmers University of Technology where HRTEM analyses of photoluminescence samples were performed.

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1999	2000	2001	2002	**Total**	Publication numbers
EPL/HUT	Ref. journal art.	1	2	5	1	**9**	1,4-7,10,13,14,17
	Ref. conf. papers	-	2	5	1	**8**	25,28,31-36
	Master degrees	-	3	1	2	**6**	39-44
LP/HUT	Ref. journal art.		1			**1**	16
	Doctoral dissert.			1		**1**	38
LPC/UH	Ref. journal art.	1	3	4		**8**	7-10,13-15,17
LEIT/UT	Ref. journal art.	1			3	**4**	2,11,12,18
	Ref. conf. papers			2	2	**4**	26,27,29,30
	Doctoral dissert.				1	**1**	37
	Master degrees		2			**2**	45,46
CEM/TUT	Ref. journal art.			1		**1**	7
	Ref. conf. papers			2		**2**	28,30

5 Other Activities

In the beginning of the project, a Project Coordination Board was formed. It consisted of the representatives of the semiconductor industry and the partner laboratories. The task of the Board was to direct the operation of the consortium. The Board had four meetings per year. In addition, three working groups of scientists were organized (Recombination Group, MEMS Group, Light from Silicon Group). The working groups were conducting the actual characterization activity. Three Annual Seminars were arranged for the staff members of the project. Typically, 20-30 persons were attending the seminars.

6 Publications

6.1 Refereed Journal Articles

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STRUCTURAL AND FUNCTIONAL APPROACH TO POLYMER MATERIALS

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Abstract

This is the interim report of the project *Structural and Functional Approach to Polymer Materials.* It contains work done during the two first years of funding. Funding is granted until the end of 2002, therefore we are not prepared to deliver a final report at this stage. We anticipate new exciting results before the end of 2002, which will be included in the report requested by the Academy of Finland in June 2003. Many of the tasks in this report are extensions to work done in the MATRA programme, the report of which is refered to as O1, Reports by the Academy of Finland, in press since June 2001.

In this consortium work we have focused our attention on several entirely new approaches to the preparation and characterisation of functionalised polymers in thin polymer membranes for applications related to the transport of charge and small species, in particular for proton or electron transport. The characterisation includes methods of modelling with statistic and molecular methods for a more precise synthesis planning in the future.

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Membranes for ion transport, especially for use in fuel cells, have been prepared by irradiation methods: direct sulfonation of proton irradiated membranes, pre-irradiation with electron beam followed by controlled “living“ free radical polymerisation, as well as entirely new catalytic processes have been developed and will be further explored. Good results with respect to mechanical properties and conductivity have been achieved. Another approach involves the synthesis of self-organising fluid like structures by coupling phenols by hydrogen bonds to sulfonic acid containing stiff molecules. Mesoscale control of the structures has been achieved.

A great deal of work is centered on the essential problem of polymer processability. The self-organising structures can be processed into layers. A dilemma of polyanilines is their total infusibility and insolubility. Efforts are put into feasible substitution to enhance solubility of these important materials. New materials are produced and tested.

1 Partners and Funding

1.1 Laboratory of Polymer Chemistry, University of Helsinki, HUPol

The research group consists of project coordinator, professor Franciska Sundholm, professor Heikki Tenhu, senior researchers dr. Igor Neelov, dr. Sirkka Maunu, post-docs dr. Vladimir Aseyev, dr. Jaana Ennari, dr. Mikael Paronen, graduate students Satu Niemelä, Sami Kotkamo, Anna Zarembo, Kati Salo (on maternity leave since 30.3.2001, replaced by student Miia Hiltunen), student Harri Jokinen

1.2 Department of Engineering Physics and Mathematics, Helsinki University of Technology, HUTPhys

The research group consists of subproject leader, professor Olli Ikkala, graduate student Matti Knaapila

1.3 Laboratory of Industrial Chemistry and Polymer Technology, Helsinki University of Technology, HUTPol

The research group consists of subproject leader, professor Jukka Seppälä, dr. Barbro Löfgren (deputy project coordinator), supervisor Ulla Hippi, graduate student Minna Annala.

1.4 Department of Physics, University of Helsinki, UHPhys

The research group consists of subproject leader, doc. Ritva Serimaa, senior researchers dr. Veli Eteläniemi, dr. Mika Torkkeli, graduate student Kaija Jokela, student Teemu Ikonen at the X-ray laboratory, and senior researchers doc. Berit Mannfors (at present at the University of Michigan, Biophysics Research Division), dr. Johanna Blomqvist, graduate student Virpi Korpelainen at the Accelerator Laboratory.

1.5 Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, HUTElectro

The research group consists of subproject leader, professor Göran Sundholm, acting professor Kyösti Kontturi and graduate student Tanja Kallio.

1.6 Department of Polymer Technology, Åbo Akademi University, ÅA

The research group consists of subproject leader, professor Carl-Eric Wilén, professor Bengt Stenlund, graduate students Svante Holmberg and Peter Holmlund.

1.7 Funding

Table 1. Funding of the project in 1000 FIM in 2000-2001 (per 31.10.2001).

Partner	Funding organisation	1999	2000	2001	2002	Total
UHPol	UH	40			145	185
	Academy	31	160			191
	Magnus Ehrnrooth Foundation	40	30	30		100
HUTPhys	HUT					
	Academy					
HUTPol	HUT	20	25	30	25*	75
	Academy	70	200	200	130*	470
UHPhys	UH	150	150	100	100*	400
	Academy	96	199	199	106*	394
	Vilho, Yrjö and Kalle Väisälä Foundation	40	40*	40		
	Ministry of Education, graduate school, material physics	200	200	200		600
HUTElectro	HUT			17		17
	Academy			170.5		170.5
ÅA	ÅA					
	Academy	90	200	200	110*	490
Total						

* not included in total sums

2 Research work

2.1 Objectives and Work Plan

The objectives of the project were defined in the original research proposal:

The main objective is to introduce functionality by design and synthesis of novel polymer materials for applications in both active and passive electronic components and microsystems. The aim is to prepare and test new nanostructured polymer materials for use in selective sensors, in optoelectronics, controlled absorption and release, and in ion and electron transport systems (power sources), as well as in insulators and encapsulants. New approaches aiming at solving interfacial contacts between incompatible polymers, and between polymers and electrode-current collector materials are developed. The apprehension of the mechanisms of transport and diffusion in polymers is another goal in the search for materials for sensors or charge transport. Polymer theory and atomistic simulation methods for complex polymer structures are developed. New potential functions for force fields are calculated. New efficient computer codes for parallel computers will be developed. These developments aim at molecular descriptions of dynamics in polymer systems, in relation to macroscopic properties. The characterisation will involve analysis of structure, conformation, molecular, supramolecular and supermolecular order, self-assembling, phase separation and compatibility. In this context advanced analytical methods are used and developed, such as solid state NMR including HETCOR and PFG experiments, static and dynamic light scattering, new experimental set ups in X-ray scattering, advanced electrochemical methods and electron microscopy.

Experimental and theoretical methods are combined to study well defined block and random copolymers, networks, branched polymers, liquid crystalline polymers and intercalation compounds to deepen the understanding of the process of formation of complex topological polymer structures, and ultimately the correlation between materials properties and and the chemical structure of the constituents. The following polymer properties are examined: composition, linearity, branching, crosslink density, length of chains between junctions, the effect of inclusion of rigid or liquid crystalline fragments, the effect of inclusion of components with hydrophobic and hydrophilic properties, special electric, dielectric or optical

properties, conductivity, selective sensor properties, and the inclusion and binding of small particles.

The work plan was outlined:

Synthesis and structure:

Architecture and functionality in membranes for charge transport in power sources, controlled release systems, sensors and optical applications, UHPol, UHPhys, HUTPhys, HUTElectro, HUTPol, ÅAPol and Electron Microscopy Unit of The University of Helsinki, UHEM.

Hydrogels with varying hydrophilicity and release properties, UHPol, UHPhys, HUTPhys, HUTPol, ÅAPol.

Smectic side chain liquid crystalline polymers for ferroelectric matrices and optoelectronics, UHPol, UHPhys, UHEM

Liquid crystalline, processable and *in situ* crosslinkable coatings for encapsulants and insulation in electronics, UHPol, VTT, UHPhys, UHEM

Rheology of electroactive reversible networks and composites, UHPol, UHPhys, HUTPhys.

Theory and molecular modelling:

Modelling of structure, conformation, transport, free volume and dynamics in complex polymer materials, UHPol, UHPhys, HUTPhys

Transport of protons, hydronium ions and water in polymer electrolyte membranes, UHPol, ÅAPol, HUTElectro
Diffusion, solubility and binding of small molecules in polymer matrices, UHPol

Phase separation, compatibility and related interfacial phenomena in copolymers, UHPol, UHPhys, HUTPol

Interfacial phenomena:

Synthetic approaches to solve interfacial and compatibility problems in electrode-ion conductor systems in power sources, hierarchical structures by irradiation induced grafting, HUTElectro, ÅAPol, UHPol, HUTPhys, UHEM, HUTPol

Construction of hierarchical structures of self assembling copolymers for sensors and optoelectronics by combining incompatible blocks through electrostatic attraction, HUTPhys, UHPol, UHPhys, HUTPol

2.2 Progress report: Common themes

Two different aspects of conductive polymers for various applications have been studied: ion-conducting systems and electron-conducting systems.

New proton conducting polymers electrolyte membranes for use primarily in the polymer electrolyte fuel cell (PEFC) have been studied.[1] These have been synthesised by several different methods. Totally new approaches have been introduced as the method of pre-irradiation grafting has been modified with Atom Transfer Radical Polymerisation (ATRP) techniques[2] and with living free radical graft polymerisation.[3] The method dominating the work within the MATRA programme (project no. 30582) the pre-irradiation grafting with styrene and subsequent functionalisation with sulfonic acid groups has been continued using seven different matrix polymers under carefully controlled conditions.[4-10, 21, 23, C1-C7, O1, O8, O9, P1, P4, P8] Another radiation initiated synthetic method recently favourably developed is the direct sulfonation of fluoropolymers. Heavy particle bombardment has been used in the initiating step.[8] The physicochemical and electrochemical properties of all the membranes produced have been studied using commercially available Nafion 105 and 117 as reference materials.

The water uptake from the vapour phase was very similar for all membranes with similar poly(styrene sulfonic acid), PSSA, content irrespective of the matrix material whereas the water uptake from liquid water was influenced by the matrix.[4, 7]

We have determined the conductivities, area resistances, the permeabilties of these membranes to the reactant gases (hydrogen and oxygen), the kinetics of the oxygen reduction reaction (ORR) and their performance in a laboratory fuel cell (max. 5 cm^2 active area).[6]

The dependence of the conductivity of the membranes on the relative humidity and temperature was also determined. The conductivity was observed to depend on the membrane thickness and the water uptake. The dependence of the conductivity on the temperature and the relative humidity was the same for all of the experimental membranes. Reactant gas permeabilities appeared to depend only slightly on the matrix material and no major differences in the Tafel slopes and exchange current densities of the oxygen reduction reaction were observed. Membranes with high water uptakes appeared to be less durable in the fuel cell than membranes with low water uptakes. Thus to prepare a membrane that is durable under the fuel cell conditions, the water uptake must remain low even at the expense of the conductivity.[1, 6, 7, 23, D3]

In order to investigate what structural changes take place in the membrane during operation in a polymer electrolyte fuel cell, PEFC, the PEFC tested membranes are further studied using confocal Raman spectroscopy (at Experimental Physics, Chalmers, Göteborg) and X-ray methods. The first results, for poly(vinylidene fluoride), PVDF, based membranes, obtained using Raman have been published.[5, C2, C3] The results show that a gradual loss of PSSA occurs, which is reflected in a decreased conductivity. The degradation is inhomogeneous and differs both over the membrane surface and through its depth. This degradation is aggravated on the cathode side of the membrane. The results of the corresponding X-ray measurements have not yet been made ready for publication.

During this work the control of the temperature and humidity of the reactant gases fed into the fuel cell has been improved leading to a better performance of the whole cell and a new fuel cell station for the measurement of the methanol permeability of our experimental membranes has been set up. This permeability is of interest for the evaluation of the suitability of the membranes for use in a direct methanol fuel cell.

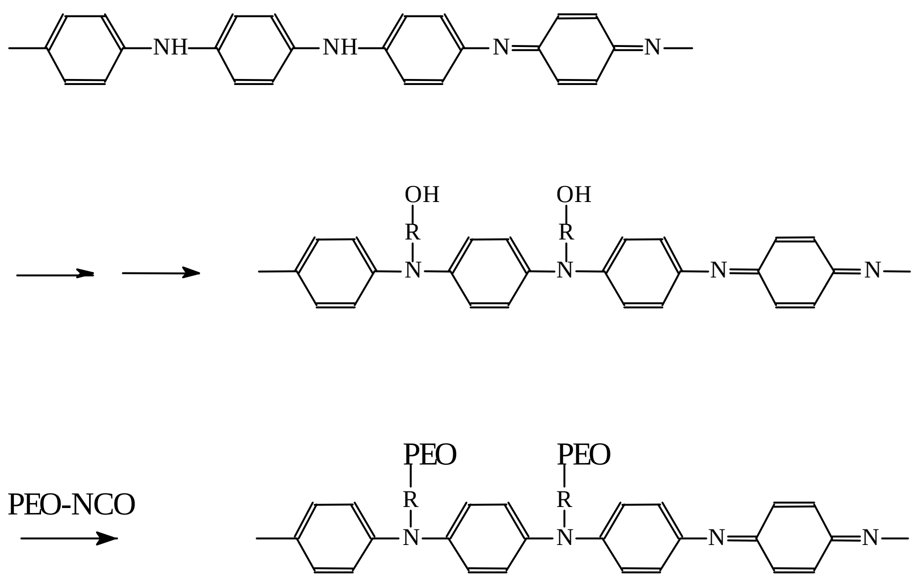
Work on electron conducting polymers is in progress in several groups, the collaboration is in its beginning.

2.3 Progress report: UHPol

Ion conducting polymers. Our studies are proceeding along three directions, very closely related, however. One major topic is the development of ion conducting membranes which is done in close connection with the groups in this consortium, thus progress is reported in section 2.2.

Electronically conducting polymers. In another approach we have been looking into methods to add processability to polymers generally considered untractable. Thus, one of the objectives is to produce water soluble polyaniline, PANI, derivatives. So far, most of such PANI derivatives have been obtained by substituting the polymer with charged groups, most commonly with sulfonic acid containing groups. In the present case the target is an electrically neutral polymer and thus, substitution of PANI with poly(ethylene oxide) (PEO) has been investigated.

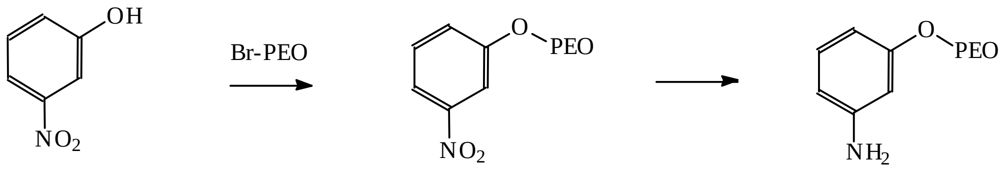
A preformed PANI was N-substituted with PEO with molar mass 5000 as follows. A N-substituted alcoholic PANI derivative was prepared, into which PEO-isocyanate was attached.



The reaction was only partially successful. Spectroscopically it could be concluded that a certain amount of PEO was attached to PANI. The degree of substitution, however, was too low to render PANI water soluble. The reason for the modest degree of substitution was most probably the low solubility of the starting material, a sample of commercial PANI.[D4]

Next, PEO substituted aniline was prepared which will be copolymerised with aniline. This method of synthesis, although requires more steps should be better in terms of conductivity of the product polymer. N-substitution generally decreases conductivity more than the substitution of the aromatic ring.

The monomer has been synthesised by substituting a 2-nitrophenol with PEO bromide, and by reducing the nitro group into an amine.



In the following step, the synthesised PEO substituted aniline will be copolymerised with aniline.

Modelling and simulation. A main line of our research is concentrated on methods to model and simulate polymer systems. Part of these studies are connected to the research on conducting polymer systems, in particular the transport of ions and small molecules in polymer electrolytes. The description of the polymer electrolyte model system has been published in several reports.[O1] Methods to predict ion conductivity in polymer electrolytes have recently been described.[O1, 18, 27]

It was shown that the conductivity also in simple systems is strongly bound to the water content of the material: thus 35 % water containing models are conductive, whereas 20 % water is not enough to support proton transport. It was found that the water distribution in the samples was quite different: in the conductive samples the water forms continuous microphases, in non-conductive materials the water is evenly distributed in the whole material as small islands.[18, 27, 33]

Distribution and transport of gases in polymer electrolytes is essential when estimating their electrochemical properties. Transport of methane, carbon dioxide, oxygen and hydrogen has been treated both by statistics and on the level of individual gas molecules. In water free materials some gases are trapped in empty holes in the matrix. These studies are in progress.

Polymer electrolyte materials with fluoropolymer matrices and sulfonic acid grafts with various water contents have been built up. As they form true models of the polymer electrolytes we have been preparing for tests in low temperature fuel cells, we will now be able to study the mechanisms of mobility and transport of charge and water on the molecular level in great detail, and hence get closer the ultimate goal of predicting membrane structures with tailored properties.

2.4 Progress report: HUTPhys

Molecular electronics continue to show challenging results, both in the field of conjugated polymers and well controlled single crystal structures of oligomers. In the field of conjugated polymers, so far the most fascinating reports discuss poly(alkylthiophenes).[O10] In all such investigations there is the inherent risk that polymer coils are formed. Therefore, even in cases when self organised structures form at a molecular length scale, the supermolecular order is poorly controlled. On the other hand, based on the oligomers, one could predict that interesting properties even in the case of polymers may emerge if such structures could be controlled at the supermolecular and macroscopic level.

We demonstrate a concept that enables nanomanufacturing based on bond reversibilty of supramolecular structures which allows the control of mesoscale structures. The concept was first demonstrated with luminescent polymers. One of the most promising polymers is polypyridine[O11, O12] which forms rod-like structures. We have constructed comb-like molecules by hydrogen bonding between hexyl resorcinol and polypyridine camphor sulfonate.[O13, 28-30] The two phenolic hydroxyls of hexyl resorcinol form hydrogen bonds to the polypyridine camphor sulfonate chain, the hexyl groups form the combs.[O13] This structure self-organises to form nanoscale structures, shown in figure 1, which are fluid like liquid crystals. The fluid properties allow orientaion of the rods *e. g.* by flow. After alignment the side groups are cleaved by heat treatment in vacuum. This renders solid films with very high overall orientation and few defects which is manifested in polarised luminescence.[29]

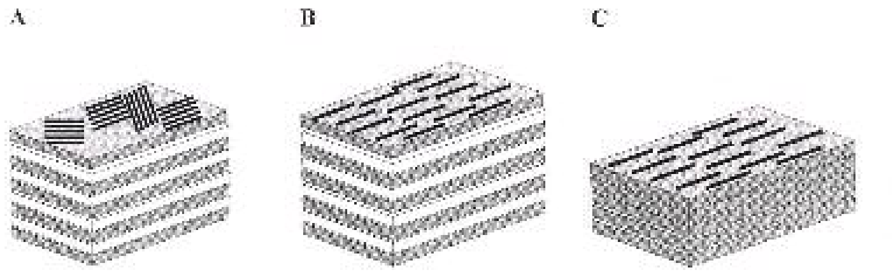


Figure 1. Hydrogen bonding hexyl resorcinol to polypyridine camphor sulfonate form comb-shaped molecules which self-organise into lamellar structures with a periodicity of 20 Å. The lamellar self-organised structure is a thermotropic liquid crystal. The rods are aligned between microscope slides. The hydrogen bonds are cleaved in a vacuum oven. Solid aligned films result.

The same preparation technique is used in an electronically conducting polymer; polyaniline. In this case the polyaniline camphor sulfonate hydrogen bonded to hexyl resorcinol forms a hexagonal array of nanoscale cylinders as shown in figure 2. This results in an increase in conductivity by two orders of magnitude.[14, 31] This emphasises the importance of control of defects in self organised structures.

Ionically conducting mesomorphic structures have been prepared by using related concepts, see figure 3.[32]

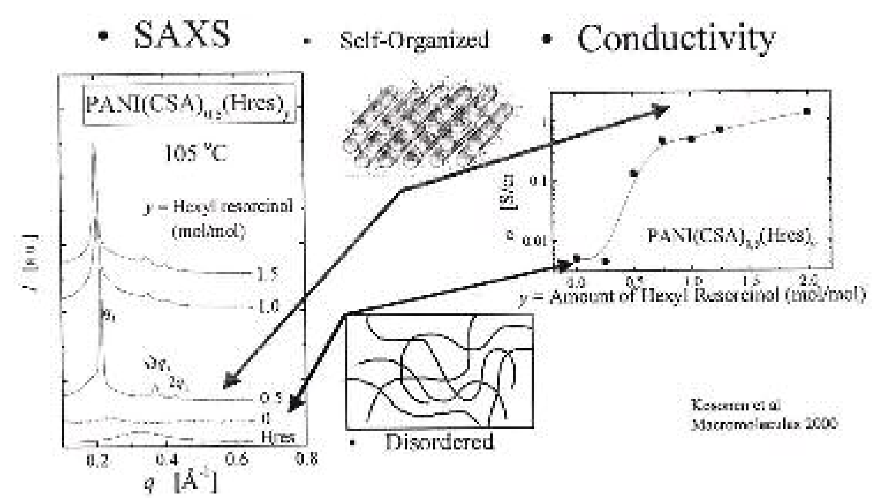


Figure 2. Processable 20-30 Å polyaniline nanocylinders based on polyaniline protonated using camphor sulfonic acid and complexed with hexyl resorcinol.[14, 31]

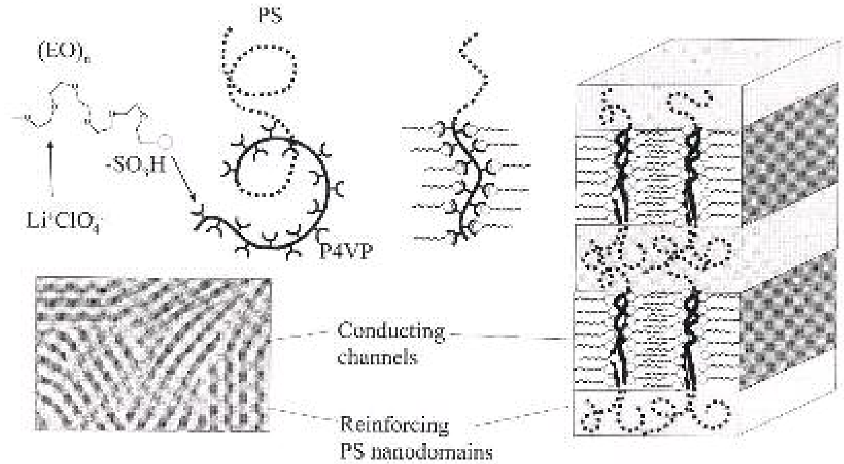


Figure 3. A concept for a molecular polymer electrolyte. The glassy around 100 Å thick polystyrene lamellae reinforce the oligomeric ethylene oxide which has been bound to the poly(4-vinylpyridine) nanoscale domains by ionic interactions.This new concept shows that polyelectrolytes can be tailored by constructing self-organising supramolecules.[32]

2.5 Progress report: HUTPol

The focus was to introduce multifunctionality by design and synthesis of novel polymer materials and composites. An ultimate goal is towards production of a conductive continuous minority phase.

The aim in our research was to develop new materials for electronics applications through compatibilised polymer blends containing a conductive polymer and a functionalised and modified polyolefin. By incorporating even a small amount of functionality, polar moieties, into the polymer chain, we were able to enhance the mixing and the interfacial adhesion between the phases.

Electronically conductive polymer blends. We studied the use of OH- and COOH-functionalised polyethylenes as combatibilisers with the polar polyaniline-complexes and a nonpolar polyethylene matrix in order to increase conductivity and/or improve mechanical properties of the blend. The compatibilisation is probably based on hydrogen-bonding interaction between polyaniline(PANI)-complex and functional groups in the polyethylene (figure 4). For the forming of hydrogen bonds PANI was doped with phenolsulfonic acid (PSA).

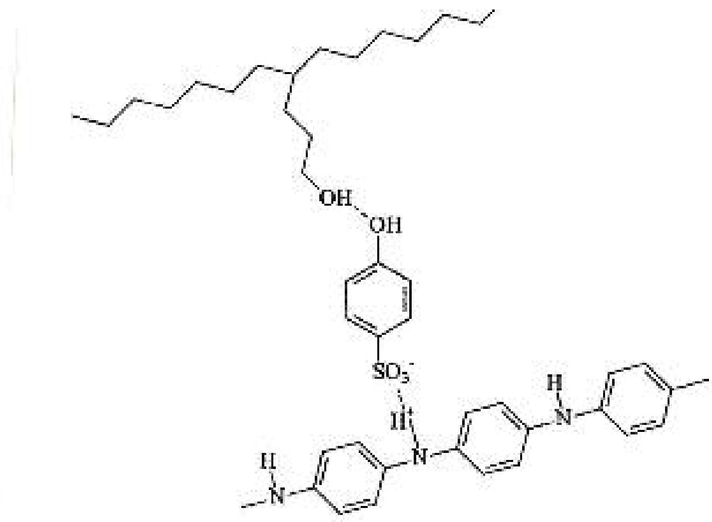


Figure 4. Hydrogen bonds between the PANI complex and functional groups in polyethylene.

For comparison PANI was doped with other sulfonic acids, which did not contain any free polar groups to form hydrogen bonds with other components in the blend.

The addition of the functionalised polyethylene improved the mechanical properties in every blend. In blends with assumed hydrogen-bonded parts conductivity did not decrease due to addition of the COOH-functionalised polyethylene.[D5]

It seems that the functionalised polyethylenes were too fluid and they could prevent PANI to percolate in the polyethylene-matrix. It is believed that the possible hydrogen bonds between PANI/PSA-complex and COOH-functionalised polyethylene diminished the negative effect of inadequate rheologies of the components.

In the near future we are going to polymerise new functional polyolefins with higher polarity, and try to find more preferable dopants for polyaniline to form hydrogen bonds with functional polymers.

Ion conductive copolymers. Polymers with protonic conductivity are useful materials for ion-exchange membranes, separators, and electrolytes in electrochemical cells. Present ionomers with high proton conductivity contain often fluorine and are very expensive, e.g. Nafion®, why new ionomers are appreciated. Such a new promising ionomer is a sulfonated metallocene copolymer, poly(ethylene-co-styrene) (figure 5).[O4-O6]

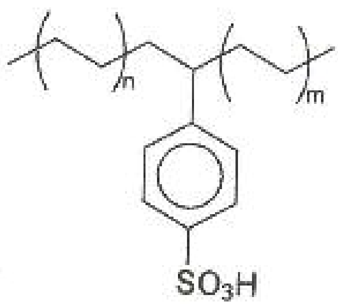


Figure 5. Poly(ethylene-*co*-styrene)

A series of copolymers have been polymerised with the styrene content from 20 mol-% to 30 mol-% in the copolymer composition. All phenyl rings in the copolymers have been sulfonated using chlorosulfonic acid as a sulfonating agent. Hot-pressed membranes have been characterised by determining water uptake and ion exchange capacity. Proton conductivity of the membranes was measured at 25 ^{o}C and in 100 % relative humidity using ac impedance method.

The preliminary studies revealed that the sulfonated copolymers have promising properties for the proton conducting applications. All the membranes had good ion exchange capacity, ca. 3,5 meq/g , and proton conductivity, ca. 120 mS/cm. The conductivity improved with increasing styrene content in the copolymer. Conductivity over 200 mS/cm was achieved at 30 mol-% styrene content. These proton conductivities are very good compared to the conductivity of Nafion 117, which had conductivity of 51 mS/cm measured at the same conditions. One drawback is reduced mechanical properties of membranes after achieving good proton conductivity. Further experiments are under way to improve mechanical properties still maintaining high proton conductivity.

2.6 Progress report: UHPhys

The aims of the study were to characterise the structure and properties of polymeric materials for electronics applications by means of X-ray scattering experiments and computational molecular modelling, based on potential energy functions. These studies are needed for understanding formation of complex structures and correlation between the properties and structures of the resulting material and its building blocks.

The materials included hairy rods, liquid crystals, and membranes for charge transport. The studies were carried out in close cooperation with the synthesis research in order to gain profound understanding of the structure and properties of the materials.

Basic research concerning development of potential energy functions to improve the description of intra- and intermolecular interactions was a part of the project.

Division of X-ray Physics. New inexpensive membrane materials were developed for fuel cell applications (UHPol). The desired properties of membranes are good conductivity, mechanical strength, and thermal stability. The matrix materials were semicrystalline polymers with a crystallinity of 40-60 %.[O1, 15, 21] The proton conducting membranes were synthesized by grafting a fluoropolymer with styrene which was sulfonated.

The matrix materials had a highly oriented lamellar structure. The sulfonated grafts were incorporated in the amorphous part of the polymer matrix. Grafting and sulfonation increased the lamellar period and decreased the average size of the crystallites.[1, 9, 10] Interestingly, the preferred orientation of the lamellae decreased only slightly due to grafting and sulfonation. In humid membranes ionic aggregates are formed.

The conductivity of the membrane depended mainly on the number of the sulfonic acid groups, their distribution and the membrane water content. For good conductions, the lamellar period increased strongly.[21] A deformable structure allows the formation of ionic aggregates and connections between them, which are necessary for good conductivity. It was observed that in the fuel cell the content of polystyrene has decreased to very low levels.[24] The lamellar distance shrinked towards the value of the pristine polymer membrane. However, scission of polymer chains may have occured which weakened the mechanical durability of the membranes.

Comb-shaped supramolecules for molecular electronics were constructed from polyparapyridine and polyaniline by using hydrogen bonds. According to X-ray diffraction experiments these self-organised to form nanoscale structures. Nanoscale conducting cylinders and layers based on self-organisation of hydrogen-bonded polyaniline supramolecules were constructed.[14, 15, 31] Poly(*para*- pyridine) based luminescent materials had a smectic liquid crystalline highly ordered three-dimensional structure. This group of materials had unique properties: they were liquid-like and allowed easy orientation of the rods on surfaces.[19, 28] Alignment in the molecular structure resulted in optical anisotropy and enhanced luminescence. The highly oriented films were studied by grazing incidence X-ray diffraction.

The Department of Physical Sciences moved to the Kumpula Campus during 2001. Because of that, no X-ray diffraction experiments could be done for 5 months. On the other hand, extra funding was obtained from the University of Helsinki for a two-dimensional detector. That finally allowed effective studies of the oriented membranes. In addition, the small-angle X-ray scattering setup was modified for grazing incidence X-ray diffraction studies of thin films.[19]

Accelerator laboratory. In force field-based simulation methods (Monte Carlo, molecular mechanics and molecular dynamics) interactions between atoms of molecular systems are described by potential energy functions (force fields). Since the properties of synthetic polymers depend strongly on the conformational statistics of the polymer chains, the reliability of the force field model used for simulations is of crucial importance. Quantum mechanical *ab initio* and density functional theory (DFT) methods can be applied in test and development of force fields through conformational studies of smaller model molecules.

The performance of the PCFF (polymer CFF) force field, which specifically is developed for synthetic polymers, was evaluated by calculating the torsional behaviour of the important chemical bonds of selected molecular systems with *ab initio* (MP2) and DFT (B-LYP and B3-LYP) methods using the standard Gaussian type basis set 6-31G(d). The molecules studied have represented model units for some commonly used polyesters[12, 25] and polyfluorides[22] such as PVDF. The severe disagreements found between the quantum mechanical and force field results have been removed by re-optimising the PCFF torsion potentials.

As applications, single chain properties such as characteristic ratios were calculated for the studied polymer chains using the modified PCFF, and the RIS Metropolis Monte Carlo method.[16, 17] The results were in agreement with the experimental values, whereas those given by the original PCFF in some cases were even contradictory to them. The modified PCFF was also applied in molecular dynamics simulations on amorphous models to study the amorphous part of the polymers in question.[20, 24] The amorphous state was of interest since, for example, in fuel cell applications the conductivity is caused by hydronium ion diffusion and proton transfer in the amorphous part of the polymer. The amorphous part of semicrystalline PVDF has been computationally studied at different temperatures, and it has been found, that both the number of free volume sites as well as the relative amount of larger sites increase at higher temperatures thus, indicating a better ability of the hydronium ions to diffuse in the material.

Plans for the EMMA-project in 2002: The study of the fuel cell tested membranes will be completed. The structure of the new polyethylene based membranes (HUTPol) will be started. The studies of the comb-shaped smectic supramolecules will be continued in co-operation with the research group at HUTPhys. Furthermore, the crystal structure of the starting material, poly(*para*-pyridine), is unknown. Its modelling has been started (co-operation with Docent Lasse Pietilä, VTT/Chemical Technology). The results will be compared with X-ray diffraction results.

2.7 Progress report: HUTElectro

Originally the research plan included three main objectives: the electrochemical characterisation of those electroactive membranes and polymers developed within the other groups of the consortium, the study of the membrane-electrode catalyst interfaces including new types of membrane-electrode assemblies and the further development of electrochemical characterisation methods for membranes.

Compared to the original plan the work has also included studies of the degradation during fuel cell runs of the radiation grafted proton conducting membranes synthesised by UHPol, but the study of membrane-electrode interfaces has not been included as the funding provided was not sufficient.

The research done on the proton conducting membranes involves the electro-chemical characterisation of these membranes. The progress is included in 2.2.

2.8 Progress report ÅA

The conventional radiation-induced grafting technique which offers little or no control over macromolecular structure has been widely used for the preparation of polymer electrolyte membranes. Recently ÅA within a collaboration with UHPol and HUTElectro has started to explore new and viable approaches to more controlled modification and functionalisation procedures of preformed partially fluorinated membranes by combining the use of pre-irradiation grafting with controlled "living" free radical polymerisation techniques.[2, 3] We have prepared membranes by grafting vinyl benzyl chloride to PVDF films using the pre-irradiation grafting method.[2] The benzyl chloride groups in the grafted PVDF function as initiators for the atom transfer radical polymerisation of styrene onto the membranes. Different ATRP systems were studied and the best one was a homogeneous system with copper bromide as catalyst. With this ATRP system the degree of polymerisation increases linearly up to at least a degree of grafting of 400 %, which implies first order kinetics as well as that this is a controlled radical polymerisation. With normal radical initiated grafting (pre-irradiation grafting) this high degree of grafting of styrene onto PVDF can not be achieved because of the high rate of termination reactions. After sulfonation the proton conductivities of the membranes are up to 70 mS cm^{-1}.

We also synthesised PVDF-*g*-(styrene-*block*-*tert*-butyl acrylate) since after sulfonation it should be possible to immobilise the precious metal catalyst to the carboxylic groups at the surface of the membrane.[2] The hypothesis is that by this the required amount of noble metal in the electrocatalyst layer could be minimised.

Plans for the EMMA project in 2002: We have started, and we will continue to exploit three different living free radical techniques that are based on the concept of dormant-active species equilibria in the preparation of improved polymer electrolyte membranes. We believe that Svante Holmberg will be able to complete his doctoral thesis within the year 2002 and Peter Holmlund to accomplish his licentiate thesis.

3 International Aspects

The international cooperation established within previous research projects supported by The Academy of Finland (MATRA no 30582) has been continued. In particular we have cooperated with Applied Electrochemistry, Royal Institute of Technology (KTH), Stockholm (Professor Göran Lindbergh). Professor G. Sundholm is part-time visiting professor at this institution since 1998. Paper C3 is a result of this cooperation.

Our collaboration within the Nordic Energy Research Programme (NEFP) has been continued. The above mentioned group at KTH is involved in this network. The Department of Experimental Physics, Chalmers University of Technology, Göteborg, Sweden (Professor Per Jacobsson), and the Department of Physical Chemistry, The Norwegian University of Science and Technology, Trondheim, Norway (graduates Preben Vie and Monica Strømgård) have been participating in the characterisation and the electrochemical tests of our membranes (see papers 5 and 23). Professor Eivind Skou at the South Denmark University in Aarhus is involved in this network, and acted as external examiner for the thesis of Nadia Walsby in August 2001.

The experiments by using synchrotron radiation were performed in cooperation with Dr. G. Goerigk, Hasylab, Hamburg, Germany. The results have been presented at several international conferences. The poly(*para*-pyridine) and the polyaniline based materials were studied in co-operation with the University of Durham, Durham, United Kingdom (Professor A. Monkman), and the University of Groningen, Groningen, The Netherlands (Professor G. ten Brinke) and personnel at the double beam line, ESRF, Grenoble, France, see papers 14, 19, 27, 28, 29, 30, 31, 32.

Extensive collaboration in the modelling and simulation work is the long established networks SUPERNET, funded by the European Science Foundation, and the INTAS 99-1114 project, see papers O1, 18, 27 and 33. Within these networks especially the collaboration with the Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia, (Dr. Igor Neelov, Professor Anatoly Darinskii) and the Solid State Physics Group at the University lof Mainz, Mainz, Germany, (Professor Kurt Binder) should be mentioned.

4 Publications and Academic Degrees

Table 2. Publications and academic degres produced in the programme.

Partner	Type of publication	2000	2001	2002	Total	Publication numbers
UHPol	Refer. papers	3	7	8	18	1-10, 21, 23,24, 27, 31, 33-35
	Ref. conf. papers		1		6	C1-C6
	M.Sc.		1		2	D4, D6
	Ph. D		1		1	D7
	Other				10	O1-O4, P1, P4, P8 P13-14 & 16
HUTPhys	Refer. papers	4	3	4	11	14, 15, 19, 24, 28-32,35, 36
	Ref. conf. papers	1			1	C8
	Ph. D.					
	Other				13	O13, O15-16, P2-3 P5-P7, P9-P11, P15-16
HUTPol	Refer. papers					
	Ref. conf. papers					
	M.Sc.	1				D5
	Ph. D., Lic.					
	Other				4	O5, O6, O14, P12
UHPhys	Refer. papers	9	13	5	27	1, 9-26, 28-32, 36
	Ref. conf. papers	2			2	C7-8
	M.Sc.					
	Ph. D., Lic.	2		1		D1, D2, D8
	Other				22	O1, O7-O9, O13 O15, P1-P11, P13-16
HUTElectro	Refer. papers	2	1	7	10	1-7, 10, 21, 23
	Ref. conf. papers		6		6	C1-C6
	M.Sc.					
	Ph. D., Lic.		1		1	D3
	Other				4	O1, O4, P13-14
ÅA	Refer. papers			2	2	2, 3
	Ref. conf. papers					
	M.Sc.					
	Ph. D., Lic.					

5 Other activities

The participants in the consortium have participated in numerous meetings, symposia and conferences, both national and international. A number of oral and poster presentations have been presented.

A Euresco conference closely related to the themes of the EMMA project was chaired in Helsinki by Franciska Sundholm in August 2001.

6 Publications

6.1 Refereed Journal Articles

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P2 M. Knaapila, J. Ruokolainen, M. Torkkeli, K. Jokela, R. Serimaa, T. Mäkelä, A.P. Monkman, G. ten Brinke and O. Ikkala: Nanostructuring of rigid electroactive polymers due to self-organization, XXXIII Annual Conference of the Finnish Physical Society, March 4-6, 1999, Turku, Finland, Turku-FL-L28 Report Series, Eds. Markus Lindberg and Ensio Laine, Abstract 10.5.

P3 J. Ruokolainen, M. Saariaho, R. Mäkinen, M. Torkkeli, R. Serimaa, E.L. Thomas, G. ten Brinke and O. Ikkala: Self-organized polymers with multiple length scales, XXXIII Annual Conference of the Finnish Physical Society, March 4-6, 1999, Turku, Finland, Turku-FL-L28 Report Series, Eds. Markus Lindberg and Ensio Laine, Abstract 10.19.

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HIGH-Q MICROMECHANICAL OSCILLATORS

Ilkka Tittonen[34].

Abstract

The objective of the project was to develop mechanical vibrating devices for sensor and some weak force detection applications and simultaneously perform basic research on physical mechanisms that cause energy dissipation in mechanical oscillators. The basic material that was chosen was single crystal silicon that was already known to have very low intrinsic mechanical energy losses due to its rigidity and perfect crystal structure. One objective was also to measure the properties of mechanical oscillators at various temperatures and under broad external gas pressure range and test various imaginable oscillator design geometries to obtain as low energy losses and high quality factor as ever possible. Major part of the work was intended to be performed by simulating the expected behaviour of each design using finite-element-method (FEM). The use of the fabricated oscillators also enabled measurements of the very fundamental measurement concept on the quantum level, meaning the limit where the quantum mechanical measurement accuracy starts to limit the measurement accuracy by disturbing the result via the quantum back action. In the final measurements, the highest Q values obtained were above 2 million in a standard manner, the thermal noise level was thus easily detectable in the resonance window and as the lastest result the linear oscillator mode high Q oscillator was designed. It is supposed to find many applications since the response is designed to be strictly linear to the weak external resonant force excitation.

1 Partners and Funding

1.1 Metrology Research Institute, Helsinki University of Technology

The research group consists of project leader professor Ilkka Tittonen, postgraduate students MSc Kaisa Nera, Lic. Tech. Kristian Lahti, Msc. Tuomas Lamminmäki, MSc Mika Koskenvuori, MSc Ossi Hahtela and student Pekka Rantakari.

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1.3 Funding

Table 1. Funding of the project in 1000 FIM in 1997-2000. Internal funding consists of manpower costs and operational expenditures provided by the organisation. The funding provided by the Academy of Finland and other external sources is also shown in the table.

Partner	Funding organisation	1999	2000	2001	2002	**Total**
HUT	Academy	315	525	495	265	**1600**
	HUT	100	150	150	100	**500**
Total		**415**	**675**	**645**	**365**	**2100**

2 Research Work

2.1 Objectives and Work Plan

1. To develop a silicon resonator with high mechanical quality factor (Q)
2. To develop a silicon resonator with high mechanical resonance frequency (f_M)
3. To develop an optical or capacitive very low noise detection system
4. To perform measurements under varying physical conditions, especially in vacuum and at low temperatures.
5. To observe new physical effects of which some are theoretically predicted but not yet experimentally discovered.

2.2 Progress Report: Common Themes

Here are the main results shortly summarized compared with the objectives

1. The highest quality factors were 2-4 million in the range of 20-50 kHz and tens of thousands in the range of 12-14 MHz, the goal was fully satisfied.
2. Highest resonance frequencies were even above 100 MHz, so the goal was well established.
3. Both capacitive and optical detection systems were built and even developed.
4. Measurements were performed in air, in vacuum and under variable pressure and in the temperature range of 4.2 - 300 K.
5. The thermal noise level was greatly reduced but the true quantum level was not yet met with a sufficient detection accuracy, but this project is still going on with the Low tenperature laboratory. On the other hand very interesting physical results were obtained by performing measurements under very short

range gas damping and under very short distance van der Waals forces. These experiements were performed by having a metallic or silicon plate very close to the oscillator itself. The theory predicts new phenomena to appear that affect the force in a nontrivial way die to the restricted geometry in the capacitance gap. In addition, a new theoretical model was developed in collaboration with the University of Konstanz and the Imperial College [2].

2.3 Progress Report: Progress by the Metrology Research Institute

High-Q micromechanical silicon oscillators

Mechanical oscillators that have a stable resonance with a high quality factor have applications as reference oscillators, sensors and even in very sophisticated high-precision experiments for observing quantum effects.

The main idea in designing a high-Q oscillator is to construct structures with low mechanical energy flow from the active resonating part of the system. Balanced torsionally vibrating structures have proved to be very promising in this respect (Fig.1). At atmospheric pressure the most significant loss mechanism is gas damping. For an oscillator working in vacuum the major part of the mechanical energy losses is caused by the coupling to the support structure and by internal friction which in turn is a result of a variety of physical mechanisms like thermoelastic effects and phonon scattering.

Figure 1. Balanced torsionally vibrating mechanical oscillator.

The influence of a dielectric coating layer on the Q-factor and the resonance frequency has been studied since the oscillators need to be coated with high-reflectivity coating in some optomechanical experiments. Since the mass of the oscillator increased due to the coating, the resonance frequency (~68 kHz) decreased by about one percent. The decreasing effect of the coating layer on the Q-factor is shown in Fig.2.

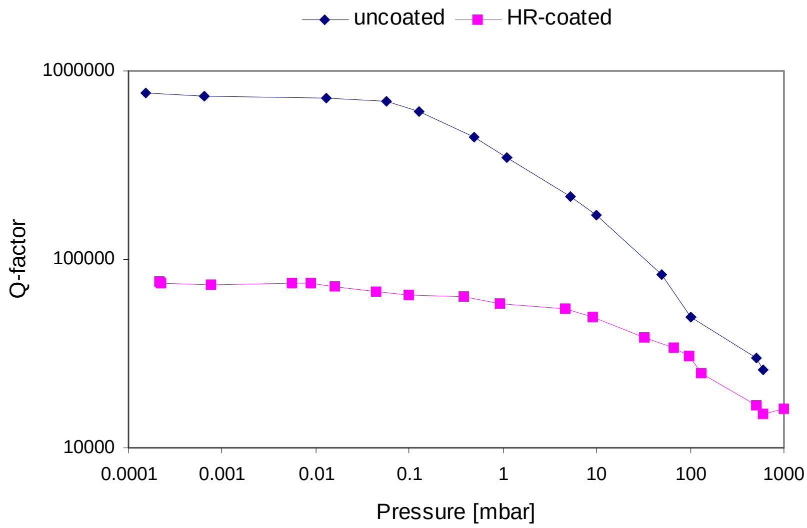

Figure 2. Influence of the high-reflectivity coating layer on the Q-factor of a mechanical silicon oscillator.

We also studied the behavior of the mechanical motion of oscillators as a function of the temperature since the physical effects that restrict the quality factor at low temperatures are rather vaguely known. In Fig.3. the Q-factor and the resonance frequency of an RF-oscillator are presented as a function of temperature. As the temperature was lowered below 50 K, the Q-factor began to increase rapidly. At 4.2 K the Q-factor was roughly three times that of the room temperature value.

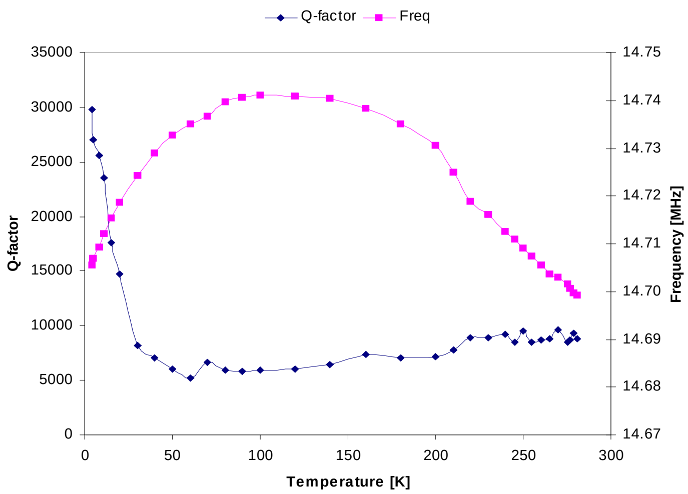

Figure 3. Q-factor and resonance frequency of a mechanical silicon oscillator as a function of temperature.

Optical interferometry on a mechanical silicon oscillator

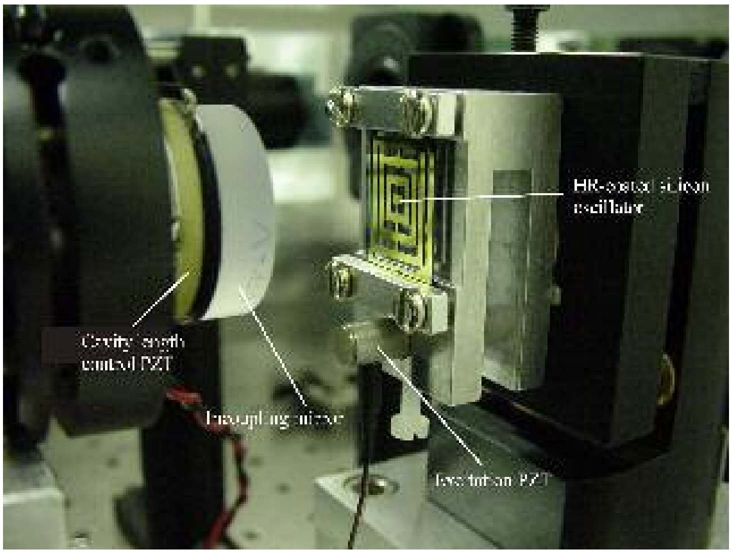

Figure 4. High-Q mechanical silicon oscillator with HR-coating (R=0.98) is employed as a planar rear mirror in a Fabry-Pérot interferometer, which has a finesse of 100, FSR of 6 GHz and an optical passband of 60 MHz.

A HR-coated high-Q mechanical silicon oscillator was employed as a planar rear mirror in a Fabry-Pérot interferometer (Fig.4). Active stabilization of the interferometer improves the stability of the resonance and makes it possible to perform sensitive interferometric measurements.

The frequency locking of a laser to an optical cavity usually requires the generation of an error signal with a typical slope at the resonance. The Hänsch-Couillaud locking method (Fig.5) utilizes polarization spectroscopy by monitoring changes in the polarization of the reflected light. A polarization analyzer detects dispersion shaped resonances, which give the error signal for the electronic servo loop. The error signal contains information about the changes in the cavity length of the optical resonator and thus the motion of the mechanical oscillator can be observed.

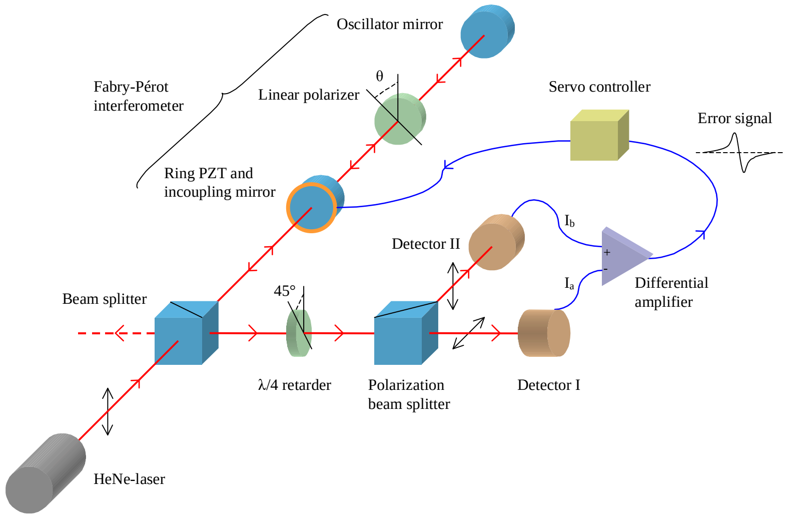

Figure 5. Hänsch-Couillaud locking method is based on the polarization spectroscopy.

The error signal was detected with the use of a spectrum analyzer. The noise floor of the interferometer response indicates that the sensitivity of the interferometer, or the minimum displacement in the oscillator position that can be detected, is Δx_{min}=1.7□10^{-14} m. This gives the optomechanical sensor a high enough sensitivity to observe for example the Brownian motion (Δx_{the}= 1.9□10^{-13} m) of the mechanical oscillator at room temperature (Fig.6).

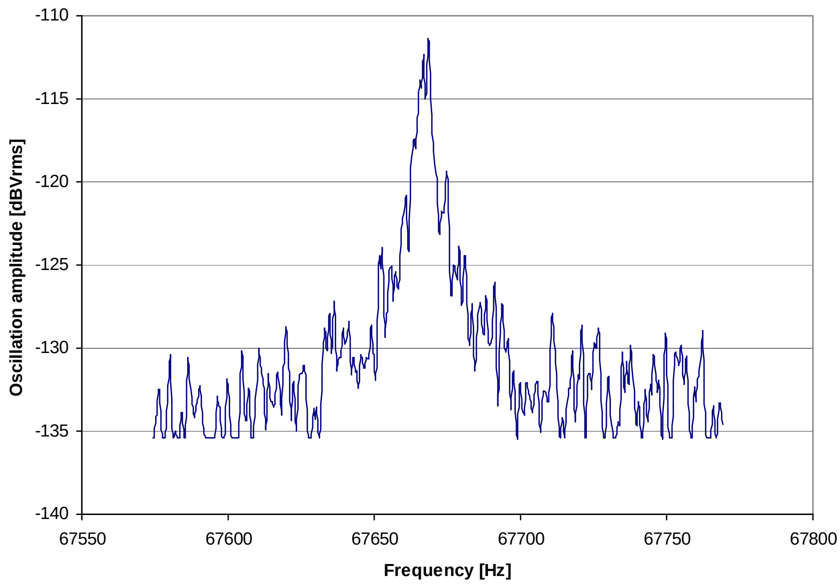

Figure 6. Thermal excitation of a high-Q oscillator was found to cause a clearly detectable interferometer signal. The corresponding displacement of the rear mirror of the cavity was 10^{-13} m.

3 International Aspects

The work was partly initiated as an international project at the University of Konstanz, so the visibility has been rather high. The most active competition has been with the optical physics research group in Paris (A. Heidmann) and M. Blencowe (University of Dartmouth) and with M. Roukes (Caltech).

4 Publications and Academic Degrees

Table 2. Publications and academic degrees produced in the project. Numbers of different types of publications are given along with the reference numbers. List of refereed journal articles are given in Section 6.1, refereed conference papers in Section 6.2, monographs in Section 6.3 and theses in Section 6.4.

Partner	Type of publication	1999	2000	2001	2002	**Total**	Publication numbers
HUT	Ref. journal art.	2	0	0	2(+3)	**4(+3)**	1-7
	Ref. conf. papers	2	2	3	1	**8**	8-15
	Monographs	-	-	-	-	**-**	
	Doctoral dissert.	-	-	-	-	**-**	
	Licentiate degrees	-		1	1	**2**	16-17
	Master degrees	1	1	2	1	**5**	18-22

5 Other Activities

Results have been reported in many silicon technology and Electronics manufacturing graduate school meetings.

6 Publications

6.1 Refereed Journal Articles

[1] I. Tittonen, T. Kalkbrenner, G. Breitenbach, T, Müller, R. Conradt, S. Schiller, E. Steinsland, N. Blanc and N. F. de Rooij,
Interferometric measurements of the position of a macroscopic body: towards observation of quantum limits,
Physical Review **A 59**, 1038-1044, (1999).

[2] K. Jacobs, I. Tittonen, H. M. Wiseman and S. Schiller,
Quantum noise in the position measurement of a cavity mirror undergoing Brownian motion,
Physical Review **A 60**, 538-548 (1999).

[3] T. Mattila, O. Jaakkola, J. Kiihamäki, J. Karttunen, T. Lamminmäki, P. Rantakari, A. Oja, H. Seppä, H. Kattelus and I. Tittonen,
14 MHz Micromechanical oscillator, Sensors and Actuators, in print.

[4] T. Mattila, J. Kiihamäki, T. Lamminmäki, O. Jaakkola,A. Oja, H. Seppä, H. Kattelus and I. Tittonen,
12 MHz Micromechanical Bulk Acoustic Mode Oscillator,
Sensors and Actuators, in print.

[5-7] Three more publications are under preparation: 1) about various designs and their physical parameters under variable conditions, 2) about measurements about the geometry where the moving oscillator has been placed very close to a surface of a metallic or silicon plate to observe effects of gas damping and short-range

interactions between the wall and the oscillator and 3) about the design and charactersitics of the new linear high-Q oscillator design

6.2 Refereed Conference Papers

[8] T. Veijola, T. Mattila, O. Jaakkola, J. Kiihamäki, T. Lamminmäki, A. Oja, K. Ruokonen, H. Seppä, P. Seppälä and I. Tittonen, *Large-Displacement Modelling and Simulation of Micromechanical Electrostatically Driven Resonators Using the Harmonic Balance Method,* Technical paper, International Microwave Symposium, IEEE Microwave Theory and Techniques Societ, Boston, June 11-16 (2000).

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[10] Nera, K., Hahtela, O., Kujala, M., Lahti, K., Lamminmäki, T., Ruokonen, K., Voipio, V. & Tittonen, I. *High-Q micromechanical silicon oscillators.* XXII International Conference on Low Temperature Physics, Helsinki, Finland, August 4-11, 1999. s. 616.

[11] Grigoras, Kestutis; Juvonen, Tuuli; Nera, Kaisa; Heikkilä, Paula; Franssila, Sami *Bulk-Micromachined Silicon Microbridges for Infrared Emitters.* Micromechanics Europe 2001, Cork, Ireland, September 16-18.

[12] Voipio, V., Nera, K., Ruokonen, K., Lamminmäki, T. & Tittonen, I. *Approximating circles by polygons in anisotropic echting of (100) silicon.* Eurosensors XIII, The Hague, The Netherlands, September 12-15, 1999. s. 531-532.

[13] Mattila, T., Jaakkola, O., Kiihamaki, J., Karttunen, J., Lamminmaki, T., Rantakari, P., Oja, A., Seppa, H., Kattelus, H. &Tittonen, I. *14 MHz Micromechanical Oscillator.* Transducers '01 Eurosensors XV, Munich, Germany, June 10-14, 2001. s. 1102-1105.

[14] Veijola, T., Ruokonen, K., Tittonen, I. *Compact model for the squeezed-film damping including the open border effects.* The 4th International Conference on Modeling and Simulation of Microsystems, 19-21.3.2001, South Carolina, USA. USA 2001, pp. 76-79.

[15] Lamminmäki, T., Ruokonen, K., Tittonen, I., Mattila, T., Jaakkola, O., Oja, A., Seppä, H., Seppälä, P. & Kiihamäki, J. *Electromechanical analysis of micromechanical SOI-fabricated RF resonators.* Third International Conference on Modeling and Simultation of Microsystems, San Diego, USA, March 27-29, 2000. s. 217-220.

6.3 Monographs

6.4 Doctoral, Licentiate, and Master Theses

[16] K. Lahti, Phase-Matching in the Optical Nonlinear Process of Second Harmonic Generation, Licentiate of Science Thesis, 10.5.2001 Helsinki University of Technology.

[17] T. Lamminmäki, Coupled Micromechanical Silicon Resonators for high-frequencies, Licentiate of Science Thesis, 6.5.2002, Helsinki University of Technology.

[18] K. Nera, Mikromekaanisen suurihyvyyslukuisen piioskillaattorin prosessointi ja mittaaminen (Fabrication and characterisation of a high-Q micromechanical silicon oscillator), Master thesis, 10.10.2000 Helsinki University of Technology.

[19] M. Koskenvuori, Mekaanisen resonaattorin toteuttaminen MHz-alueelle SOI-teknologialla (Realization of a mechanical resonator in the MHz-range using SOI-technology) Master thesis, 18.2.2002 Helsinki University of Technology.

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[22] O. Hahtela, Optical interferometry on a mechanical silicon oscillator, Master thesis, 3.12.2001, Helsinki University of Technology

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Digital frequency stabilization of a Nd:YAG solid state laser using high finesse optical resonator as a reference.
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[29] Lahti, K., Vahala, E., Heiliö, M., Kasvi, A. & Tittonen, I.
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XXXIV Annual Conference of the Finnish Physical Society, Espoo, Finland, March 9-11, 2000. paper 2.4.

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Laser frequency stabilization using a phase modulation scheme.
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Finite element method simulations on micromechanical sensors.
XXXIII Annual Conference of the Finnish Physical Society, Turku, Finland, March 4-6, 1999. paper 10.18.

[32] Seppälä, P., Jaakkola, O., Karttunen, J., Kiihamäki, J., Lamminmäki, T., Mattila, T., Oja, A., Ruokonen, K. & Seppä, H.
Micromechanical resonators: Fabrication and characterization.
The XXXIV Annual Conference of the Finnish Physical Society, Espoo, Finland, March 9-11, 2000. paper 5.20.

In response to the proposal of the Research Council for Natural Sciences and Engineering, the Board of the Academy of Finland decided on 9 June 1998 to launch National Research Programme on Electronic Materials and Microsystems. The objective of the programme was to promote basic research leading to new innovative applications; to support the ongoing research and development effort within the Finnish electronics and electrical industry; and to support applied research funded by the Technology Development Centre and the Finnish industry. At the same time, the programme supported the development of research environments within university units, which is crucial to improving researcher training opportunities. Finally, the programme hoped to encourage science students working in such fields as physics, chemistry and mathematics to turn their attentions increasingly to industrial applications.

The budget of the National Research Programme on Electronic Materials and Microsystems was 30 MFIM (5,1 MEUR). Eleven research projects were funded employing about 50 full time researchers and large number of part time researchers. This research report collection includes reports by all of the 11 projects and gives an overall picture of the level of electronic materials and microsystems research in Finland.

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