



IMEL - NCSR "DEMOKRITOS"

CENTER OF EXCELLENCE IN MICRO, NANOTECHNOLOGIES AND MICROSYSTEMS

Annual Report

2004

Aghia Paraskevi, Athens GREECE www.imel.demokritos.gr

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PREFACE

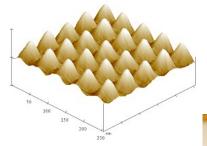
The Institute of Microelectronics (IMEL) is one of the 8 Institutes of the National Center for Scientific Research (NCSR) "Demokritos". It started its activities in 1985 and in the year 2001 it has been designated by the General Secretariat for Reasearch and Technology after evaluation by an International Scientific committee as the National Center of Excellence in Micro- and Nanotechnologies, Nanoelectronics and Systems, with full capability in silicon processing and in micro and nanofabrication, characterization and testing, as well as in design, modeling and simulation of materials, structures devices circuits and systems. The developed expertise, know-how and infrastructure at IMEL place it as a highly competitive institution at European level. Its role for the country is unique in promoting high technology development in the field of Micro and Nanotechnologies, the transfer of technology and know-how to the industry and the development of human potential in the above fields.

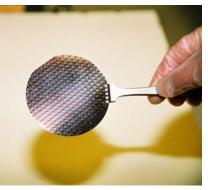
IMEL, through its long trajectory in research and technology, it has developed important competitive advantages as follows:

- Excellence in Research and Technology
- Critical mass of high level scientists and engineers, with experience and expertise in Micro, Nanotechnologies and systems
- Important technology and know-how and important proprietary result covered by corresponding patents
- Infrastructure and facilities

With the above infrastructure, expertise and know-how, IMEL is fully competitive at EU level and it has the potential to act at national level as a nucleus of the Micro and Nanotechnology activity and as a catalyst for high technology industrial development.

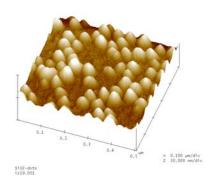
In this annual report, the research and education activities of IMEL are presented, together with the main achievements and results in the year 2004.



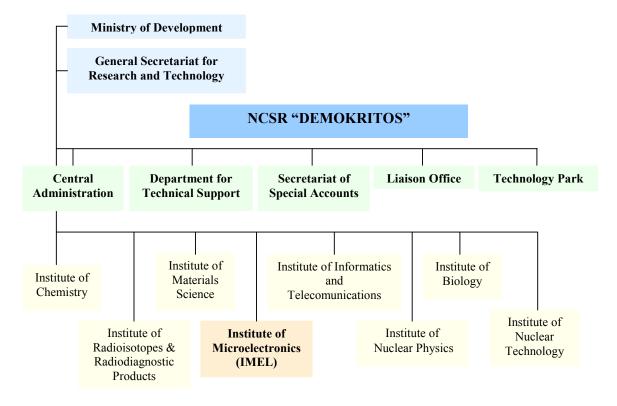


The Director of IMEL

Dr A. G. Nassiopoulou



ORGANIZATIONAL STRUCTURE OF NCSR "DEMOKRITOS"





ORGANIZATIONAL STRUCTURE OF IMEL

Director: Dr. A.Nassiopoulou

Deputy Director: Dr. K. Misiakos

Institute International Scientific Committee Prof. D.Antoniadis, Prof. C.Claeys, Prof. P.Fauchet, Prof. D.Ioannou, Prof. G.Kamarinos, Prof. S.Pantelidis

> Institute Administration & Technical Support

Director Advisory Board President: P. Normand Dr. P.Argitis, Dr. E.Gogolides, Dr. S.Katsafouros, Dr. K.Misiakos

Education & Training Dr. N.Glezos, Dr. N.Papanikolaou Dr. A.Tserepi

Program I Micro &Nanofabrication

Project I. 1 Lithographic Polymers & Processes Project leader: Dr. P. Argitis

Project I. 2 Plasma Processing & Simulation for Micro & Nano Patterning Project leader: Dr. E.Gogolides

Project I. 3 Front-end Processes for Micro & Nanfabrication Project leader: Dr. C.Tsamis

Project I. 4 Thin Films by Chemical Vapor Deposition (CVD) Project leader: Dr. D.Davazoglou Program II Nanostructures & Nanoelectronic Devices

Project II. 1 Low Dimensional Semiconductors Science & Applications Project leader: Dr. A.Nassiopoulou

Project II. 2 Silicon Nanocrystal Memories Project leader: Dr. P.Normand

Project II. 3 Molecular Materials as Components of Electronic Devices Project leader: Dr. N.Glezos Program III Silicon Sensors & Microsystems

Project III. 1 Micromachined Silicon Sensors & Microsystems Project leader: Dr. A.Nassiopoulou

Project III. 2 Bio-microsystems Project leader: Dr. K.Misiakos

Project I. 3 Thin Film Devices for Large Area Electronics Project leader: Dr. N.Kouvatsos

Project III. 4 Circuits & Devices for Optoelectronic Interconnections Project leader: Dr. G. Halkias Services in Micro, Nanotechnology & Nanosystems

Project leader: Dr. A Nassiopoulou Scientist in Charge: E. Tsoi



INFRASTRUCTURE and FACILITIES

The infrastructure available at IMEL is unique in Greece and it includes state-of-the art equipment and facilities for both micro and nanofabrication in a clean room area, and for design, modeling, characterization and testing of materials, devices, circuits and systems. A great part of the infrastructure has been funded through competitive projects at National and European level. The clean room of a total area of 300m² has been fully upgraded in the year 2002.





IMEL AT A GLANCE

Main objectives of IMEL

The main objectives of IMEL are as follows:

- Long-term research. Development of fundamental knowledge.
- Development of novel technologies, processes and high added-value technology products.
- Development of human potential through educational and training activities.
- Services in advanced technologies and transfer of technology to the industry.

Research activities

IMEL's focus in Research activities is in the following fields:

- A. MICRO and NANOFABRICATION
 - Lithographic Polymers and Processes
 - Plasma Processing and Simulation for Micro and Nano Patterning
 - Front-end Processes for Micro and Nanodevices
 - > Thin Films by Chemical Vapor Deposition (CVD)
- B. NANOSTRUCTURES and NANOELECTRONIC DEVICES
 - Low Dimensional Semiconductors Science, Technology and Applications
 - Silicon Nanocrystal Memories
 - > Molecular Materials as Components of Electronic Devices

C. SILICON SENSORS and MICROSYSTEMS

- Micromachined Silicon Sensors and Microsystems
- ➢ Bio-microsystems
- > Thin Film Devices for Large Area Electronics
- Circuits and Devices for Optoelectronic Interconnections

Research at IMEL is carried out within competitive National, European and International projects and direct contracts with industry as for example with Intel, Sharp, Photronics etc.

Education activities

Due to its unique infrastructure at a national level and the important expertise and know-how of its researchers, IMEL plays an important role in post-graduate education. It participates very actively in the following educational programmes, in collaboration with Greek universities, by providing special courses and laboratory training:

- 1. Post-graduate program in "Microelectronics" in collaboration with the University of Athens (for MSc and PhD degrees)
- 2. Post-graduate program in "Microsystems and Nanoelectronic devices" in collaboration with the National Technical University of Athens.
- 3. Post-graduate program in "Nanosciences and Nanotechnologies" in collaboration with the University of Thessaloniki.

Personnel

The personnel of IMEL (see annex II) is a total of 58 people including 16 research scientists and engineers, 30 post-doctoral scientists and Phd students and 12 technicians and administrative personnel and on contract.

Budget

The direct budget of the Institute not including the overhead of NCSR "Demokritos", was in 2004 on the order of 2.4 M \in from which 41% was from the regular public budget, 53% from competitive EU and national projects and 6% from contracts with industry.

MAIN RESEARCH RESULTS

PROGRAM I: MICRO AND NANOFABRICATION

Project I. 1: LITHOGRAPHIC POLYMERS and PROCESSES Project leader: P. Argitis

Project I. 2: LITHOGRAPHY and PLASMA PROCESSING FOR NANO-PATTERNING Project leaders: E. Gogolides

Project: I. 3: FRONT-END PROCESSES FOR MICRO and NANOFABRICATION Project leader: C. Tsamis

Project: I. 4: THIN FILMS BY CHEMICAL VAPOR DEPOSITION (CVD) Project leader: D. Davazogou

PROGRAM II: NANOSTRUCTURES and NANOELECTRONIC DEVICES

Project II. 1: SEMICONDUCTOR NANOSTRUCTURES: SCIENCE & APPLICATIONS Project leader: Dr A. G. Nassiopoulou

Project II. 2: SILICON NANOCRYSTAL MEMORIES Project leader: P. Normand

Project II.3: MOLECULAR MATERIALS as COMPONENTS of ELECTRONIC DEVICES Project leader: N. Glezos

PROGRAM III: SILICON SENSORS and MICROSYSTEMS

Project III. 1: MICROMACHINED SILICON SENSORS and MICROSYSTEMS Project leader: A. G. Nassiopoulou

Project III. 2: BIO-MICROSYSTEMS Project leader: K. Misiakos

Project III. 3: THIN FILM DEVICES for LARGE AREA ELECTRONICS Project leader: D. N. Kouvatsos

Project III. 4: CIRCUITS and DEVICES for OPTOELECTRONIC INTERCONNECTIONS Project leader: G. Halkias

PROGRAM I MICRO and NANOFABRICATION

Project I. 1: LITHOGRAPHIC POLYMERS and PROCESSES

Project leader: P. Argitis

Other key researchers: I. Raptis, E. Gogolides, K. Misiakos

Post-doctorals: A. Douvas, M. Vasilopoulou, D. Goustouridis

Graduate students: M. Chatzichristidi, D. Niakoula, N. Vourdas, P. Economou, M. Kitsara, A.Kokkinis

Projects Running:

- 157 CRISPIES, Critical issues for 157nm lithography, EU IST, E. Gogolides
- SOARING, Source optics and resists for EUV lithography, EU IST, E. Gogolides
- INTEL- MoleEUV, συμβόλαιο συνεργασίας για EUV resists, E. Gogolides
- Microprotein, Micron scale patterning of protein and DNA chips, EU Growth, P. Argitis
- Sub HTS-, Submicron patterning of High Temperature Superconducting thin films, NATO Science for Peace
- More Moore, EU FP6 Integrated Project (IST)
- Nano2Life, EU FP6 Network of Excellence (NMP)

<u>Goals:</u>

- Design and development of new resists capable for sub 100nm lithography following the roadmaps of Semiconductor Industry Association on the miniaturization of CMOS circuits
- Development of new lithographic schemes and appropriate polymeric materials for microsystem fabrication, with emphasis in the area of bio-microsystems
- Basic physicochemical studies and optimization of resist processing using standard and novel techniques and instrumentation

<u>Main results:</u>

a) New resist materials for CMOS processing

i. Polyhedral Oligomeric Silsesquioxane (POSS) - based resist platform for 193 nm and 157 nm lithography

A. Douvas, N. Vourdas, D. Niakoula, E. Tegou, V.Bellas, M. Vasilopoulou, E. Gogolides and P. Argitis

In the context of the research program for the development of new resist materials for the miniaturization of CMOS circuits new resist platforms are investigated. During the last couple of years one of the resist platforms under investigation is that based on polymers containing Polyhedral Oligomeric Silsesquioxane (POSS) groups. This work started for application in 157 nm lithography but lately, due to the last worldwide developments regarding the future of lithographic techniques, the same platform was also investigated for 193 nm lithography. The influence of the copolymer composition and the resist formulation parameters on lithographic performance was studied. Emphasis was given to the development of lithographic materials that can be used under typical processing conditions preferred by the semiconductor industry and by using standard processing equipment. Thus materials that can be processed in 0.26 N TMAH developers were developed. The lithographic evaluation was carried out at IMEC, Leuven, Belgium, in the context of the EU IST research project CRISPIES. In addition the pattern transfer properties of POSS-based resists for bilayer lithography were investigated in collaboration with the University of Nantes, France, in the context of the same project. Lithographic results obtained at IMEC under 193 nm exposure are presented in *fig. 1.1.1*.

In addition to the above a new research effort started in collaboration with the Department of Chemistry, University of Athens, for the synthesis of novel POSS units, functionalized with acid cleavable groups that could find also applications in lithographic material development.

Finally, possible applications of POSS partially fluorinated polymers as low k dielectric materials have been investigated. In this case the patterning capability can offer additional advantages.

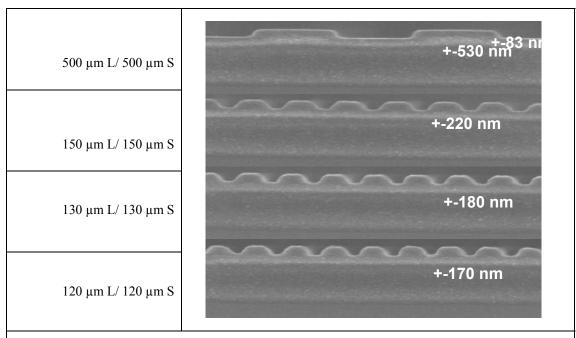


Fig. 1.1.1: Results from the lithographic evaluation of POSS-based materials at IMEC under 193 nm exposure. Exposure dose: 8 mJ/cm²

ii. New molecular materials based on polycarbocycle derivatives for line edge rouhness reduction under EUV exposure

D. Niakoula, N. Vourdas, I. Raptis, E. Gogolides and P. Argitis

A new resist platform was introduced by our group, based on the use of organic molecules synthesized by the Organic Synthesis group of the Physical Chemistry Institute. The new molecules contain functionalized polycarbocycle units and are suitable for the formulation of molecular glasses that can be exposed at EUV (13 nm). The physicochemical properties of these materials, including film formation capability, film homogeneity, adhesion to different substrates, glass transition temperature and thermal stability, have been investigated and suitable molecules that can be used in lithographic applications have been developed. First lithographic evaluation has been carried out at NCSR Demokritos under deep UV and e-beam exposure. Outgassing studies have been carried out at National Hellenic Research Foundation and first EUV exposure experiments at EPRPA, France. A first generation of such resist materials was also sent to USA and evaluated at Sandia Labs, (imaging properties under EUV exposure) and at University of Wisconsin (outgassing). The obtained results proved the viability of this approach for developing molecular resist materials. Equal lines and spaces up to 110 nm were obtained. The above work has not been published yet since a searching for possible patent filing is under way.

b) Novel lithographic processes and materials for emerging applications

i. Development of lithographic processes for biological patterning

M. Chatzichristidi, A. Douvas, P. Economou, K. Misiakos and P. Argitis

In the context of our research program (in collaboration with the Institute of Radioisotopes and Radiodiagnostic products with the support of EU Growth project "Microprotein") for novel lithographic processes aiming at biomolecule patterning, optimized processes and new materials were developed.

First, it was proved that the resist-based multi step lithography under biocompatible conditions proposed by our group for biomolecule patterning is capable for the fabrication of submicron protein microarrays. By using a near UV contact aligner (exposure at 310 nm) the fabrication of microarrays with spot dimensions down to $0.5 \,\mu$ m was achieved.

Second, new resist platforms were investigated for lithography under biocompatible conditions. A new material with promising lithographic properties that can be used for protein patterning has been selected. In addition materials that could be more suited for oligonucleotide patterning have been also developed.

In addition to the resist-based methodology the use of laser polymer ablation for biomolecule patterning has been investigated in collaboration with the excimer laser laboratory of National Hellenic Research Foundation and the University of Rovira I Virgili, Taragona, Spain. The possibility for using a biopatterning process based on this approach was demonstrated.

A Workshop on multianalyte biosensing devices was also co-organized with the University of Rovira I Virgili, in Tarragona, Spain in February 2004.

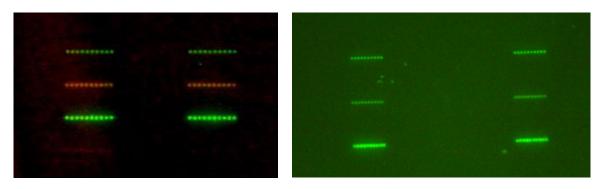


Fig. 1.1.2: Protein microarrays fabrication with our resist-based lithographic methodology. **Left:** Rows of 1,5 μ m dots. Three proteins coupled with their counterparts, which are labeled with different fluorescent markers are shown. **Right:** 0.75 μ m dot arrays of the same protein fabricated in 3 successive lithographic cycles are shown.

ii. Thick film patterning technologies for the fabrication of microsystems

I. Raptis, M. Kitsara, M. Chatzichristidi, P. Argiti and D. Niakoula

The research activities in this area focused on a) the transfer of a high aspect ratio patterning process for Proton Beam micromachining and b) the design and implementation of a process for the fabrication of closed microchannels

a) In collaboration with the Institute of Nuclear Research, Hungarian Academy of Sciences a high aspect ratio micromachining process with proton beam exposure was established. In this technology the negative aqueous base developable chemically amplified resists developed at IMEL were used and structures with lateral dimension $<10\mu$ m and aspect ratio =6 (*fig. I.1.3*) were revealed. This study was carried out within the framework of a Greece-Hungary bilateral cooperation project.

b) A novel complete patterning technology for the fabrication of closed micro channels was developed. The resist used in this technology is based on epoxy-based polymers and suitable photoacid generator. The fabrication of the closed channels is performed through UV exposure on two different negative chemically amplified resist films. Using this technology closed micro channels with length up to 3200µm and width up to 800µm were fabricated and the water flow was proved.

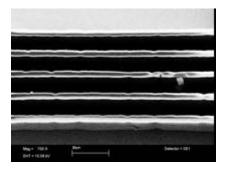


Fig. 1.1.3: Top down SEM image from resist structures with critical (lateral) dimension $5\mu m$ and aspect ratio = 6 Resist ADEPR. Exposure 2MeV protons. Exp. dose 344 nC/mm²

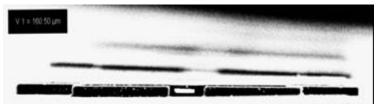


Fig. 1.1.4: Typical closed microchannel from epoxy- based resists. Length 800µm width 200µm

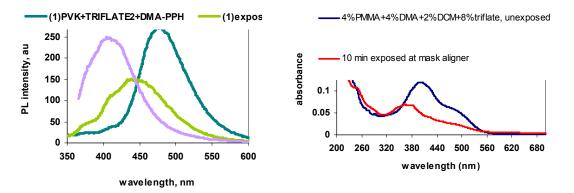
iii. Novel patterning scheme for photonic applications

M. Vasilopoulou, D. Georgiadou and P. Argitis

A new research activity has started during the last year aiming at the use of photochemically induced material transformations in polymers for use in photonic applications.

In particular this work focuses on the use of photochemically induced emission tuning for the definition of different colour emitting areas in polymeric layers. This capability was demonstrated first in non-conducting polymer matrices and it is extended now in conducting ones and in the fabrication of OLEDs with the aim to define in one polymer layer the three primary colour emitting pixels (Red-Green-Blue). The same approach is also investigated for white light applications.

We have prepared electroluminescent devices emitting blue colour (λ_{max} =413 nm) based on commercially available poly (9-vinylcarbazole) (PVK), which is well known for efficient energy transfer and devices where we introduced a dispersed dye (1-[4-(dimethylamino) phenyl]-6-phenylhexatriene) (DMA-DPH) and a photoacid generator (of the series of onium salts) in the polymeric layer. By using an appropriate photochemical transformation through a photomask in a single layer, we were able to change the colour to desirable direction, since the parent compound and its photochemical product have distinguishable luminescence spectra (green and blue colour respectively). A series of different photoacid generators were investigated for use in this application. In fig. 1.1.5, the photoluminescence spectra of PVK added DMA-DPH before and after exposure at appropriate wavelength (248 nm) are shown. Possibilities for the definition of three primary colours are investigated by using also a red fluorescent dye 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylamino-styryl)-4H-pyran (DCM) in the same marix (fig. 1.1.6).



DMA-PPH emission spectrum.

Fig. 1.1.5: Photochemically induced shift of Fig. 1.1.6: Characteristic absorption spectrum changes of the two fluorescent dyes inserted in a host polymeric material before and after the irradiation.

c) Characterization of thin polymeric films suitable for high resolution lithogarphy

I. Raptis, P. Argitis, E. Gogolides, D. Goustouridis, D. Niakoula, N. Vourdas and A. Kokkinis

Measurement of Glass transition temperature i.

Within the research project MoreMoore (IP funded from EU) and with collaboration with Clariant the evaluation of the OPTI methodology developed at IMEL (fig. 1.1.7) was carried out and the principle of operation was proved. Using this methodology several acrylate based polymers and resists suitable for EUV lithography were successfully characterized (fig. 1.1.8). The evaluation of these materials showed that glass transition temperature of films depends on the film thickness and on the processing conditions (PAB temperature etc). In addition for 'thick' polymeric films (>500nm) the glass transition temperature proved to be very close to the DSC values.

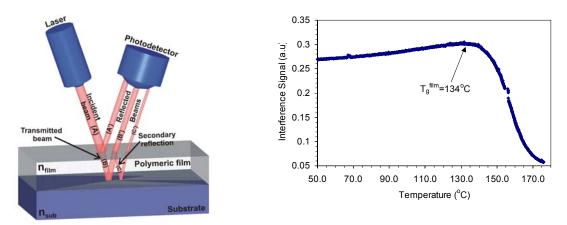


Fig. I.1.7: OPTI (Single wavelength **Optical** Interferometry) principle of operationi. MMC2 film on Si substrate.

Fig. 1.1.8: Interferogram in the case of 400nm thick

ii. Dissolution properties of thin polymeric films

A complete methodology for the monitoring of dissolution of thin (40nm - 3000nm) polymeric films was designed and implemented. This methodology is based on a) white light interferometry (470-750nm) using properly stabilized light source and high resolution spectrometer with fiber optic input (fig. 1.1.3) and b) home made software for the in-situ evaluation of polymeric film thickness from the each time interference spectrum (fig. I.1.4)).

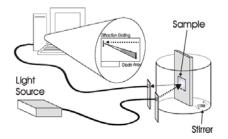


Fig. I.1.9: Multiwavelength dissolution rate monitoring apparatus.

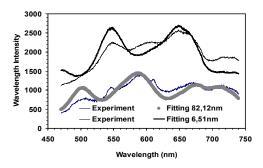


Fig. I.1.10: Comparison between experimental and fitted, with intereference equation, spectrums at two instances.

PUBLICATIONS in INTERNATIONAL JOURNALS

- "Polyhedral oligomeric silsesquioxane (POSS) acrylate copolymers for microfabrication: properties and formulation 1 of resist materials", E. Tegou, V. Bellas, E. Gogolides and P. Argitis, Microelectronic Engineering, 73/74, 238-243, (2004)
- 2. "Polyhedral oligomeric silsesquioxane (POSS) based resists: material design challenges and evaluation at 157 nm", E. Tegou, V. Bellas, E. Gogolides, P. Argitis, D. Eon, G. Catry, C. Cardinaud, Chem. Mater. 16, 2567-77, (2004)
- "Glass transition temperature monitoring in bilayer and patterned photoresist films", D. Niakoula, I. Raptis, D. 3. Goustouridis, P. Argitis, Jpn. J. Appl. Phys., 43 (8A), 5247-8, (2004)
- 4. "Surface segregation of photoresist copolymers containing polyhedral oligomeric silsesquioxanes studied by X-ray photoelectron spectroscopy", D. Eon, G. Cartry, V. Fernandez, C. Cardinaux, E. Tegou, V. Bellas, P. Argitis, E. Gogolides, J. Vac. Sci. Technol. B, 22, 2526-32, (2004)
- "Evaluation of poly (hydroxyethyl methacrylate) imaging chemistries for micropatterning applications", M. 5 Vasilopoulou, S. Boyatzis, I. Raptis, D. Dimotikalli, P. Argitis, J. Mater. Chem., 14, 3312-20, (2004)
- 6. "Development and molecular-weight issues on the lithographic performance of poly (methyl methacrylate)", A. Olzierski, I. Raptis, Microelectron. Eng. 73-74 244-251 (2004)
- "Resists for nanolithography", P. Argitis, Encyclopedia of Nanoscience and Nanotechnology, H.S. Nalwa ed., 7 American Scientific Publishers, (March 2004)
- "157 nm Laser Ablation of polymeric layers for fabrication of biomolecule microarrays", Douvas, P.S. Petrou, S.E. 8 Kakabakos, K. Misiakos, P. Argitis, Z. Kollia, E. Sarantopoulou, A. C. Cefalas, Anal. Bioanal. Chem., accepted for publication
- 9 "Proton beam micromachining on strippable aqueous base developable negative resist", I. Rajta, E. Baradacs, M. Chatzichristidi, E. S. Valamontes, I. Raptis, accepted for publication at Nucl. Instrum. Meth. B

PRESENTATIONS in CONFERENCES

- "Sub 10 μm Protein Microarrays Fabricated Using New Near UV Photoresist and Novel Multi-Step Lithographic Scheme", M. Chatzichristidi, A. Douvas, K. Misiakos, I. Raptis, C.D. Diakoumakos, P. Petrou, S. E. Kakabakos, P. Argitis, 2nd International Workshop on Multi-Analyte Biosensing Devices, Tarragona, Spain, 18-19 of February 2004
- "157 nm laser ablation of polymeric layers for fabrication of biomolecule microarrays", P. Petrou, A. Douvas, S. E. Kakabakos, P. Argitis, K. Misiakos, E. Sarantopoulou, Z. Kollia, A. C. Cefalas, 2nd International Workshop on Multi-Analyte Biosensing Devices, Tarragona, Spain, 18-19 of February 2004
- "Fabrication of Microscale Protein Arrays for Low Crosstalk Electrochemical Sensing", Bush, I. Katakis, M. Chatzichristidi, K. Misiakos, P. Argitis, 2nd International Workshop on Multi-Analyte Biosensing Devices, Tarragona, Spain, 18-19 of February 2004
- "Dissolution properties of ultrathin photoresist films for the fabrication of nanostructures", A. Kokkinis, E. S. Valamontes, I. Raptis, 2nd Conf. on Microelectronics Microsystems and Nanotechnology (11/2004, Athens)
- "Characterization of various low-k dielectrics for possible use in applications at temperatures below 160°C", M. Vasilopoulou, S. Tsevas, A. M. Douvas, P. Argitis, D. Davazoglou and D. Kouvatsos, 2nd Conf. on Microelectronics Microsystems and Nanotechnology (11/2004, Athens)
- 6. "Photochemically Induced Emission Tuning of Conductive Polumers used in OLEDs", M. Vasilopoulou, G. Pistolis and P. Argitis, 2nd Conf. on Microelectronics Microsystems and Nanotechnology (11/2004, Athens)

PATENTS

E. Gogolides, P. Argitis, E. Couladouros, V. Vidali, M. Vasilopoulou, G. Cordoyanis, "Polycarbocyclic derivatives for modification of resist optical and Etch resistance properties", European Patent granted, International Patent number, PCT/EP02/12284, WO 03/038523, 18/12/2003

Ph. D. THESES

- V. Bellas, Department of Chemistry, University of Athens, February 2004 Thesis title: "Development of novel siloxane and silsesquioxane polymeric materials for high resolution lithography. Structure-properties relationships" Advisor: Dr P. Argitis
- M. Chatzichristidi, Department of Chemistry, University of Athens, December 2004 Thesis title: "Chemically amplified photoresist materials for the fabrication of microsystems" Advisor: Dr P. Argitis

PROGRAM I MICRO and NANOFABRICATION

Project I. 2: LITHOGRAPHY and PLASMA PROCESSING FOR NANO-PATTERNING

Project leaders: E. Gogolides, A. Tserepi

Other key researchers: K. Misiakos, N. Glezos

Post-doctorals: G. Patsis, E. Tegou, V. Constantoudis

PhD candidates: G. Kokkoris, P. Bayiati, N. Vourdas

MSc Students: V. Sarris

External collaborators: A. Boudouvis (NTUA), P. Leunissen (IMEC), Th. Christopoulos (U. Patras), Y. Wang, J. Roberts (INTEL)

Projects Running:

- EU, 157 CRISPIES, Contract Nº: 30143
- EU, SOARING, Contract Nº: 35254
- INTEL-MoleEUV
- Nano2life EU Network of Excellence
- PHOTRONICS

Objectives:

During 2004 our nanopatterning activity focused in the metrology, characterization and simulation of Line Edge or Line Width Roughness (LER, LWR) for sub-100nm CMOS lithography and Etching. Our LWR metrology software is now friendly and robust, and it is thus used by other laboratories such as IMEC and INTEL. Our stochastic Lithography Simulator is also now a fast tool for investigation of process and material effects on LWR. In addition plasma etching of ultra thin photoresist films has proven that the etching rate drops as the photoresist thickness is reduced, thus alleviating some etch resistance demands of ultra thin films.

A significant advancement was also the completion of an integrated topography simulator for microelectronics and Microsystems fabrication. This work opens new possibilities in the simulation of plasma processes and process design and optimization.

During 2004 the group has also focused its activity in the fabrication of polymer-based microfluidics for biomicrosystems (Programme III. 2 led by Dr K. Misiakos). Polydimethylsiloxane as well as PolyMethylMethAcrylate were patterned both with soft lithography and classical lithography followed by plasma etching. We expect that this growing activity will soon become a program on its own.

Main results:

a) NANO-PATTERNING

i. Metrology and Characterization of Line Width Roughness using fractal concepts

V. Constantoudis, G. Patsis and E. Gogolides (Collaboration with P. Leunissen, Y. Wang, J. Roberts)

The resist Line Width Roughness (LWR) is one of the major obstacles to the development of new generation lithograpies since it causes local deviations of the gate length from the nominal value and thus degradation effects on transistor performance. The control and reduction of LWR necessitates first a reliable and complete methodology for its measurement and characterization.

Such a methodology has been developed during last years in the Institute and has been realized in a software written in MATLAB platform. The methodology is based on off-line analysis of top-down CD-SEM images of the resist patterns and, in fact, consists of two steps. First, through an image analysis algorithm the edges of the lines contained in the image are extracted, and then their roughness (LER) is characterized using a set of parameters.

ii. 3D Stochastic Lithography Simulator incorporating a Modified Dissolution Algorithm based on Critical Ionization Model

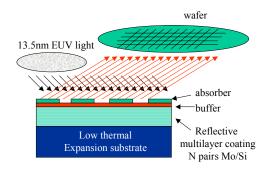
G. Patsis, V. Constantoudis, V. Sarris and^{*} E. Gogolides

A fast (quasi-static) dissolution algorithm was developed based on the concept of critical ionization, and added in the simulation flow of the other modules of the general lithography simulator we have been developing. Specifically, our objective is to obtain the suitable set of material and process parameters that minimize the line-edge roughness (LER) for a given material and process conditions.

iii. Simulation of electron beam exposure for EUV mask fabrication

G.Patsis and N. Glezos

Extreme-ultraviolet- (EUV) mask *fabrication (fig. 1.2.1)* using electron-beam lithography has to eliminate the proximity effect defects, for the accurate representation of the patterned features. One special characteristic of EUV masks is that they contain a multilayer stack of repeated Si/Mo thin layers. This has to be considered explicitly in the simulation of electron-beam energy dissipation calculation using Monte Carlo methods (*fig. 1.2.2*). In a first approximation to the problem of electron scattering in a multi-layer substrate, the continuous slowing down approximation utilizing the Rutherford differential cross section is used in order to describe the electron inelastic energy loss mechanism and determine the amount of deposited backscattered energy, in the resist film on top of the multi-layer substrate. Three-dimensional modeling is used and in a first approximation, no secondary electron generation or other excitation processes are considered. The effect of the number of layers and their relative thickness in terms of incident electron energy is investigated (*fig. 1.2.3*).



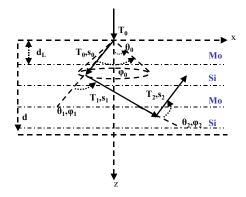


Fig. 1.2.1: Simplified picture of the lithographic process in EUVL. The main characteristic of the mask is that it is reflective rather than transmissive, because in the specific radiation wavelength all components of the mask absorb.

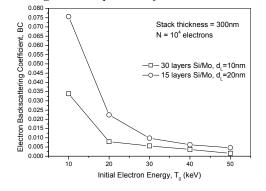


Fig. 1.2.2: Coordinate system used in the electron track simulation. Between successive scattering events, energy loss is calculated from the continuous slowing down approximation.

Fig. 1.2.3: Backscattering coefficient vs. electron beam energy as obtained from the simulation of $N=10^5$ electrons penetrating a 300nm multiplayer Si/Mo stack on top of a Si-substate.

iv. Plasma Etching of Ultra Thin Photoresist Films for Nanolithography

N. Vourdas, E. Gogolides

Recently, the requirements of microelectronics fabrication and nanotechnology imposed the thorough study of thin and ultra-thin films. Several set of experiments have already advocated that properties of thin films can be completely different from those of the bulk material. We focused on the plasma etching behavior of thin polymeric films, and shown a clear dependence of etch rate on the initial polymer thickness: etch rate decreases as the initial polymer thickness decreases, i.e. the etch resistance of thin polymeric films is higher

than that of bulk polymer. In order to explain these results we correlated the etch rate profile to the T_g profile vs. polymer thickness. It is shown that T_g of thin films is different, in general, from the T_g of the bulk material. These differences in T_g indicate differences in structural and physical properties (conformation, orientation, density etc) vs. polymer thickness. These differences are reflected as different behavior during plasma treatment and subsequently as different etch rate. These findings, i.e. increased etch resistance of thin films, slightly alleviate the demands for etch resistance of ultra thin photoresist films of the next generation lithography. Finally, these results suggest that ER of thin films should be referred to specific thickness.

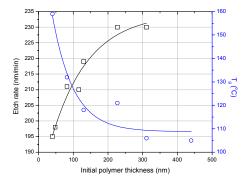


Fig. 1.2.4: ER and Tg variation of PMMA $(M_n=15k)$ layers on Si as a function of initial polymer thickness.

b) Integrated simulation of topography evolution during plasma etching of structures in MEMS and microelectronics fabrication

G. Kokkoris and E. Gogolides

A simulation framework has been developed for the topography evolution of features etched with plasma. This framework links the bulk plasma gas phase with the profile of the etched feature and constitutes of: a) The local flux calculation model. Shadowing and reemission of flux are taken into account. b) The surface etch model. This model includes the processes during the etching of SiO_2 and Si surface with fluorocarbon plasma. c) The algorithm for the topography evolution of the etched features. The level set method is implemented.

The aim of the simulation framework is to contribute to the profile control of the etched structures, which is necessary for the efficient operation of the corresponding microelectronic devices and MEMS. The simulation framework has been applied to SiO_2 and Si feature etching with fluorocarbon plasmas. Etching artifacts, such as RIE lag and microtrenching are predicted and explained in SiO_2 feature etching. The framework is also applied to *a*) the simulation of the multiple step, deep Si etch process (Bosch process, *c*) and *b*) the simulation of the roughness evolution of etched Si surfaces.

c) MICROFLUIDICS

i. Fabrication of Microfluidic channels on PMMA substrates

N. Vourdas, A. Tserepi and E. Gogolides (collaboration with Prof. Th. Christopoulos)

The fabrication of microfluidic devices with features of 10-1000um size are of great importance in many fields of analytical science, where a small quantity of sample is available, enhanced resolution and sensitivity in separation is needed and increased functional integration is desired (medical, chemical and biochemical analysis, microchemistry etc).

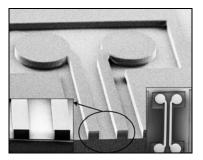
We explore a new method for fabrication of microfluidic devices based on the plasma etching of polymers using an appropriate mask (1. photosensitive silicon-containing polymeric mask (poly-dimethylsiloxane-PDMS), 2. aluminum mask). Plasma etching rates (ER) of PMMA were measured via in situ spectroscopic ellipsometry in order to achieve maximum ER_{PMMA} . Through this technique, an 80um-depth channel has been formed on PMMA, for application to DNA analysis device via capillary electrophoresis.

ii. Fabrication of PDMS Microfluidic devices

E. Vlachopoulou, A. Tserepi, K. Misiakos and E. Gogolides

Poly-Dimethyl Siloxane (PDMS) has been proved very popular elastomer material, widely used in the fabrication of microfluidic devices. For PDMS patterning, soft lithography has been overwhelmingly used, realized by means of thermal crosslinking of the material already shaped in molds made out of polymeric or other materials. Our work aims, through our familiarization with the current state-of-the art in soft lithography, at the development of alternative PDMS patterning technology based on plasma etching.

Soft lithography based on the SU (8) resist and a thermally-crosslinked PDMS, in combination with plastic bonding techniques have been developed at IMEL for the fabrication of PDMS microfluidic devices. At the same time, plasma-based PDMS patterning was optimized to proceed with high speed and to yield properly designed wall profiles for the etched structures. The evaluation of both techniques, soft lithography and plasma-based patterning, are to be compared on a simple microfluidic device consisted of a channel extending between two circular receptors for the external tubing used for fluid delivery to the microfluidic device (see figures below). This device is expected to be used for biological solutions delivery on a biosensor developed at IMEL.



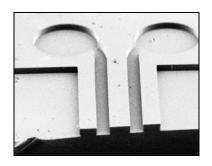


Fig. 1.2.5: SEM image of the lithographically-defined SU-8 structure. Thickness 100 μ m, width of lines 150 μ m. The vertical profile of the lines is clearly shown at the inset on the left, while a top-down SEM of the whole structure is shown at the inset on the right.

Fig. 1.2.6: SEM image of the replica PDMS structure, fabricated by soft lithography. Depth of micro-channels 100 μm, width 150 μm. Diameter of the reservoirs: 800 μm.

iii. Electrowetting-based technology for actuation in microfluidics

P. Bayiati, A. Tserepi, K. Misiakos and E. Gogolides

Hydrophobic polymeric films deposited on various surfaces (by plasma deposition or by spin-coating of teflon-like commercial products) can be used for the fabrication of microfluidic devices based on electrowetting. Such surfaces can be varied from hydrophobic to hydrophilic with voltage application and thus they can be used for actuation of fluid transport in microchannels. For the plasma deposition of the hydrophobic films, fluorocarbon gases, such as C_4F_8 , are used and the plasma parameters are investigated in order to obtain films with high hydrophobicity and low contact angle hysteresis. However, such hydrophobic films have poor dielectric properties, a problem which can be overcome by the use of composite multilayer structures, where the hydrophobic film is combined with a material of good dielectric constant and strength, such as Si_3N_4 . Reversible, low voltage electrowetting has been achieved with the use of a composite film consisted of a thin hydrophobic fluorocarbon material deposited on a Si_3N_4 film (*Figs. I.2.7*). Furthermore, electrowetting experiments were conducted (*Fig. I.2.8*) using protein solutions on Teflon spin-coated surfaces and exhibited significant and reversible dynamic contact angle modulation indicating that such hydrophobic films can be used in microfluidic channels for biological fluid transport based on the electrowetting on dielectric effect.

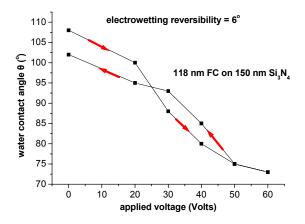


Fig. 1.2.7: Water contact angle of fluorocarbon plasma deposited film in combination with a Si_3N_4 film versus applied voltage (first increasing and then decreasing).

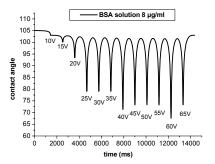


Fig. 1.2.8: Contact angle modulation of a teflon spin-coated surface on Si_3N_4 during application of pulses of increasing voltage, using a bovine serum albumin solution.

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- "Line Edge Roughness (LER) investigation on chemically amplified resist (CAR) materials with masked helium ion beam lithography", S. Eder-Kapl, H. Loeschner, M. Zeininger, O. Kirch, G. P. Patsis, V. Constantoudis, and E. Gogolides, Microelectronic Engineering, 73-74, 252 (2004)
- "Photoresist line-edge roughness analysis using scaling concepts", V. Constantoudis, G. P. Patsis, and E. Gogolides, J. Microlithogr. Microfabrication, Microsyst. 3, 429 (2004)
- "Effects of photoresist polymer molecular weight on line-edge roughness and its metrology probed with Monte Carlo simulations", G. P. Patsis, V. Constantoudis, and E. Gogolides, Microelectronic Engineering 75(3), 297 (2004)
- "Line edge roughness and critical dimension variation: Fractal characterization and comparison using model functions", V. Constantoudis, G. P. Patsis, L. H. A. Leunissen, and E. Gogolides, J. Vac. Sci. Technol. B (22), 1974 (2004), and Virtual Journal of Nanoscale Science & Technology- August 30, 2004, Volume 10, Issue 9
- 5. "Si etching in high-density SF₆ plasmas for microfabrication: Surface roughness formation", E. Gogolides, C. Boukouras, G. Kokkoris, O. Brani, A. Tserepi, V. Constantoudis, Microelectronic Engineering 73-74, 312 (2004)
- "Oxygen plasma modification of polyhedral oligomeric silsesquioxane (POSS) containing copolymers for micro and nano fabrication", N. Vourdas, V. Bellas, E. Tegou, O. Brani, V. Constantoudis, P. Argitis, A. Tserepi, E. Gogolides, Plasma Processing Of Polymers, pp. 281-292, (2004)
- "Simulation of SiO₂ and Si feature etching for microelectronics and MEMS fabrication: a combined simulator coupling modules of surface etching, local flux calculation, and profile evolution", G. Kokkoris, A. Tserepi, A. G. Boudouvis, and E. Goggolides, J. Vac. Sci. Technol. A 22, 1896 (2004)
- "Si etching in high-density SF₆ plasmas for microfabrication: surface roughness formation", E. Gogolides, C. Boukouras, G. Kokkoris, O. Brani, A. Tserepi, and V. Constantoudis, Microelectron. Eng. 73-74, 312 (2004)
- "Selective Plasma-induced Deposition of Fluorocarbon Films on Metal Surfaces for actuation in microfluidics", P. Bayiati, A. Tserepi, E. Gogolides, K. Misiakos, J. Vac. Sci. Technnol. A 22(4), 1546-1551, (July/August 2004)

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- 1. "Material origins of line-edge roughness: Monte Carlo simulations and scaling analysis", G. P. Patsis, V. Constantoudis, and E. Gogolides, **Proc**. SPIE Int. Soc. Opt. Eng. 5376, 773 (2004) (Poster)
- "Toward a complete description of linewidth roughness: a comparison of different methods for vertical and spatial LER and LWR analysis and CD variation", V. Constantoudis, G. P. Patsis, L. H. A. Leunissen, and E. Gogolides, Proc. SPIE Int. Soc. Opt. Eng. 5375, 967 (2004) (Poster)
- "Effects of different processing conditions on line-edge roughness for 193-nm and 157-nm resists", M. Ercken, L. H. A. Leunissen, I. Pollentier, G. P. Patsis, V. Constantoudis, and E. Gogolides, Proc. SPIE Int. Soc. Opt. Eng. 5375, 266 (2004) (Poster)
- 4. "Increased plasma etch resistance of thin polymeric and photoresist films", N. Vourdas, E. Gogolides, A. G. Boudouvis, *Proceedings of Micro & Nano Engineering (MNE)* 2004, Rotterdam-Netherlands, 19-22 September 2004
- "Characterization of the roughness of structures and surfaces through SEM and AFM images", V. Constantoudis, G.P. Patsis, E. Gogolides, A. Tserepi, E. Valamontes, and O. Brani, *Proceedings of the XIX Panhelenic Conference* of Solid State and Materials Science, 2004 (in Greek)
- "Modification of the morphology of Si-contained polymer surfaces after plasma treatment", A. Tserepi V. Constantoudis, G. Cordoyiannis, E. Valamontes, N. Vourdas and E. Gogolides, *Proceedings of the XIX Panhelenic Conference of Solid State and Materials Science*, 2004 (in Greek)

CONFERENCE PARTICIPATION

- "Line Width Roughness (LWR) metrology, characterization, and simulation: Developing the software tools for understanding, describing, and predicting LER", E. Gogolides, V. Constantoudis, G. P. Patsis, *EUVL Workshop* 2004, Roterdam, 23/9/04 (Poster)
- "Calculations of electron-beam energy deposition in resist films over multiplayer Si/Mo substrates", G. P. Patsis, N. Glezos, *Microfabrication, Microsystems and Nanotechnology (MNN)*, Athens, 2004. (Talk)
- 3. "Effects of polymer chain architecture on film surface and line edge roughness. Monte Carlo Simulations", G. P. Patsis, and E. Gogolides, *Microfabrication, Microsystems and Nanotechnology (MNN)*, Athens, 2004. (Poster)
- "Plasma etch rate measurements of thin PMMA films correlation with the glass transition temperature", N. Vourdas, A. G. Boudouvis, E. Gogolides, 2nd Conference on Microelectronics, Microsystems and Nanotechnology (MMN2004), Athens, Greece, November 15-17, 2004

- "Patterning of thick polymeric substrates for the fabrication of micrifluidic devices", M.E. Vlachopoulou, A. Tserepi, N. Vourdas, E. Gogolides and K. Misiakos, 2nd Conference on Microelectronics, Microsystems and Nanotechnology (MMN2004), Athens, Greece, 15-17 November, 2004
- "Electrowetting of plasma-deposited hydrophobic films as a means for fluid transport in microfluidics", A. Tserepi, P. Bayiati, K. Misiakos, E. Gogolides, 4th Int. Meeting on Electrowetting, Blaubeuren, Sept. 2004 (poster)
- 7. "Complexity in Science and Society" Patras, July 2004 (poster: "Fractal structures in nanoelectronics") (best poster award)
- 8. "Fractal polymer surfaces after lithographic processing", XX Panhelenic Conference on Solid State and Materials Science, Ioannina September 2004
- "Profile evolution during SiO₂ and deep Si feature etching", G. Kokkoris, A. G. Boudouvis, and E. Gogolides, 16th International Vacuum Congress, Venice, Italy, June 28 - July 2, 2004

INVITED TALK

"Determining the impact of statistical fluctuations on resist line-edge roughness", L.H.A. Leunissen, M. Ercken, G. P. Patsis, *Micro and Nanoengineering (MNE)*, Roterdam (2004) (Invited talk)

PROGRAM I MICRO and NANOFABRICATION

Project: I. 3: FRONT-END PROCESSES FOR MICRO and NANOFABRICATION

Project leader: C. Tsamis

Other key researchers (From the Institute): P. Normand Post-doctorals: D. Skarlatos, E. Kapetanakis PhD candidates: N. Kelaidis, A. Chroneos External Collaborators: D. Tsoukalas (NTUA), V. Valamontes (TEI of Athens)

Projects Running:

- EU, IST 2000-30129 FRENDTECH

Objectives

- Study of dopant diffusion/activation and point/extended defect kinetics in Group-IV semiconductors (Silicon, Strained Silicon, etc.) for CMOS applications
- Thermal processes for ultra-thin gate dielectrics (oxides, oxynitrides) in Group-IV semiconductors for CMOS applications
- Process optimization for Nanodevices (Fabrication, Electrical Characterization)
- Continuum and atomistic simulation of processes and devices

Research activities and main results within 2004

a) High quality ultra-thin oxides by oxidation of very low energy nitrogen-implanted silicon

Oxidation of nitrogen-implanted silicon is one of the techniques used during the last decade for the fabrication of reliable nitrogen-rich ultra-thin (<4nm) thermal SiO₂ layers necessary as gate dielectrics in deep submicron CMOS technology.

During the last years, we performed a systematic study on the influence of nitrogen implantation conditions on thermal oxidation and on the defect formation during oxidation of nitrogen-implanted silicon substrates. Based on this study we proposed a methodology that results in the **formation of high quality ultra-thin oxides** and in the **total suppression of extended defects in the substrate**.

Within this year we have studied the electrical characteristics of the oxides as well as the influence of the oxidation on point defects kinetics.

i. Electrical characterization of ultra-thin nitrided oxides

D. Skarlatos, E. Kapetanakis, N. Kelaidis, C. Tsamis, P. Normand and D. Tsoukalas

The electrical properties of ultra-thin (2.5-3nm) oxides grown under the same oxidation but various implantation conditions as a function of the nitrogen distribution were investigated. SIMS measurements showed that a lower content of nitrogen remains within the oxides formed using low energy (3 keV) as compared to the medium energy (25 keV), explaining the dependence of the oxide thickness on the implantation energy (*Fig. I.3.1*). On the other hand, oxides formed by very low energy implantations show superior electrical characteristics in terms of interface surface states and leakage currents (*Fig. I.3.2*), due to the suppression of extended defects in the silicon substrate.

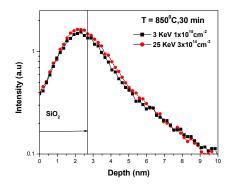


Fig. I.3.1: Nitrogen distribution of oxides grown under the same oxidation but different implantation conditions.

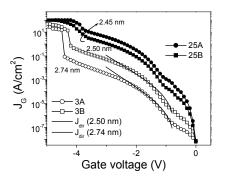


Fig. 1.3.2: Reduced leakage currents are measured for oxides formed with very low energy nitrogen implantation, due to the suppression of extended defects in the silicon substrate.

ii. Interstitial injection during oxidation of nitrogen-implanted silicon

D. Skarlatos, C. Tsamis and D. Tsoukalas

It is known that oxidation of silicon causes interstitial injection into the silicon substrate, which enhances the diffusivity of dopants, as boron and phosphorus (Oxidation Enhanced Diffusion or OED). Systematic studies of OED during oxynitridation in N_2O ambient showed that a higher number of interstitials is injected compared to common oxidation in dry oxygen ambient at the same temperature regime. This is attributed to the presence of the interfacial nitrogen, which affects the kinetics of interstitial injection.

We studied interstitial injection during the oxidation of nitrogen implanted silicon, using buried Boron δ -layers to monitor interstitial supersaturation. In contrast to N₂O oxidation, *no difference in Boron diffusivity enhancement was observed compared to dry oxidation of non-implanted silicon*. A possible explanation is that the implanted nitrogen acts as a sink for the injected interstitials during its non-Fickian diffusion towards the surface.

b) Interstitial injection during Arsenic diffusion

C. Tsamis, D. Skarlatos and V. Valamontes

High-dose, low energy arsenic implantation is a process that is typically used for the formation of S/D regions in silicon transistors. Compared to other dopants such as boron and phosphorus, fewer studies have been performed for the Transient Enhanced Diffusion (TED) of arsenic, mainly because these effects are of moderate intensity at high temperatures and are more significant for very shallow junctions. In addition, research on As is generally associated with high concentrations, where Fermi level dependence of dopant diffusion and point defects introduced by clustering or precipitation complicates the analysis of the implantation-induced TED.

Within this year, we investigated the damage generated by low-energy high dose As implantation performed at room temperature. The approach consists in monitoring the diffusion of the Arsenic profile as well as of Boron profile in buried δ -doped layers (*Fig. I.3.3*). The experimental results showed that the contribution of the implantation damage to the TED of As and B is not the main one. On the contrary, interstitial injection due to arsenic clustering is more important for the present conditions. From the analysis of the diffusion profiles we have estimated the value of the supersaturation ratio of silicon interstitials, consistent for both dopants (*Fig. I.3.4*).

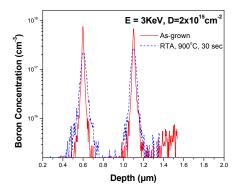


Fig. I.3.3: SIMS profile of the buried Boron δ -layers before (solid line) and after As implantation and annealing (dash line)

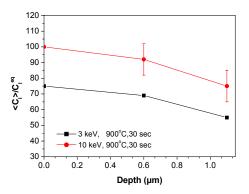


Fig. I.3.4: Supersaturation ratio of silicon interstitials as a function of the As implantation energy. A consistent value has been obtained after the analysis of As profile and boron δ -layer profile.

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- "Nitrogen distribution during oxidation of low and medium energy nitrogen implanted Silicon", Skarlatos D., Perego M., Tsamis C., Ferrari S., Fanciulli M. and Tsoukalas D., Nuclear Instruments and Methods in Physics Research, B 216, p.75-79, (2004)
- "Oxidation of nitrogen implanted silicon: Comparison of nitrogen distribution and electrical properties of oxides formed by very low and medium energy N₂⁺ implantation", Skarlatos D., Kapetanakis E., Normand P., Tsamis C., Perego M., Ferrari S., Fanciulli M. and Tsoukalas D., *Jour. Appl. Physics*, 96 (1), p. 300-309 (2004)

PARTICIPATION in CONFERENCES

- 1. "Formation and characterization of ultrathin oxides formed by oxidation of very low energy nitrogen implanted silicon", Skarlatos D., Kapetanakis E., Normand P., Tsamis C., Tsoukalas D., Perego M, Ferrari S., Fanciulli M. and Stoemenos J., 13th MEL ARI NID Workshop, 4-6 February 2004, Athens, Greece (poster presentation)
- "Point defect injection during diffusion of low energy As-implanted silicon", Tsamis C., Skarlatos D., Tsoukalas D., Ben-Assayag G., Claverie A. and Lerch W, Second Conference on Microelectronics, Microsystems, Nanotechnology, MMN 2004, 15-17 November 2004, Athens, Greece (poster presentation)

PROGRAM I MICRO and NANOFABRICATION

Project: I. 4: THIN FILMS by CHEMICAL VAPOR DEPOSITION (CVD)

Project leader: D. Davazogou

Post-doctorals: V. Vamvakas PhD students: G.Papadimitropoulos Master students: V. Assimakopoulos, D. Economou Undergraduate students: S. Tsevas, C. Favre

Projects Running:

- PROTEAS PV System (EU)

Objectives:

The objectives of this group include research and development in the following:

- a) Process and material development
- b) Characterization of CVD films

c) Applications

Main results in 2004

a) Characterization of CVD films

V. Vamvakas

The distribution of the Si-O-Si angles in SiO_2 films is obtained using FTIR transmission and reflection measurements at vertical and oblique incidence.

Of the main achievements of this year was the development of a theoretical model in order to describe FTIR transmission and reflection under oblique incidence. Using this model the refractive index of SiO₂ films was extraxted at various angles. Results for films deposited from SiH₄+O₂ are shown in *fig. I.4.1*.

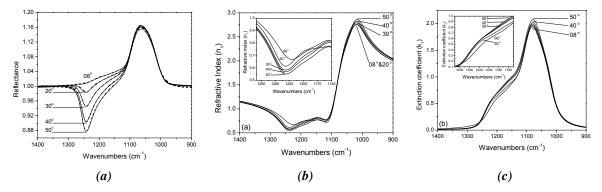


Fig. I.4.1: (*a*, left) Measured reflection spectra (broken lines) and simulated ones (continuous lines) taken on a SiO₂ film with thickness equal to 95.0 nm deposited from SiH₄+O₂ at 425 °C. The angle of incidence varies between 08 ° and 50 °, (*b*, center): Real part of the refractive index and (*c*, right): Imaginary part calculated from spectra at various angles.

Moreover, the Si-O-Si angles distribution was calculated for SiO₂ films deposited from TEOS vapors at temperatures varying between 650 and 820°C. It was suggested that in SiO₂ films exist Si-O-Si chains similar to those that exist in the bulk material (bulk-like bridges) and others attributed to chains located near grain boundaries and interfaces (boundaries-like bridges). For the former the Si-O-Si angles are smaller than for the latter. In *fig. 1.4.2* the Si-O-Si angle distributions for a TEOS deposited film at 710°C before and after annealing at 950°C are shown. It can be observed that the population of bulk-like bridges (symbolized with T4) increases with annealing and this is connected with the improved electrical properties of annealed TEOS films.

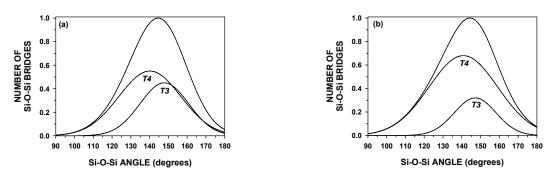


Fig. 1.4.2: Normalized Si-O-Si angle distributions (in arbitrary units) in TEOS SiO₂ films as deposited (*left*), and after annealing at 950°C (*right*).

b) CVD of SnO₂

C. Favre

This activity is related to the atmospheric pressure CVD of SnO_2 . A new APCVD reactor has been installed for the deposition of SnO_2 films from $SnCl_4$ vapors and the investigation of the capabilities of this tool (film uniformity, doping, etc) are under investigation. Another subject under investigation is the reversible changes observed in the resistivity of SnO_2 films (when activated with some gold mono-layers) as a function of their chemical environment. Gas-sensing configurations based on SnO_2 films deposited with this system are shown in *fig. I.4.3*.



Fig. 1.4.3: Gas sensors formed by depositing the heating element on a patterned SnO_2 film. The heating elements have line widths of 2 (left), 4 (center) and 6 μ m (right).

c) Local formation of Cu₂O

G. Papadimitropoulos

The oxidation of Cu lines with nano-dimensions to form locally a Cu₂O dot is a very interesting subject since this last is a p-type semiconductor and the oxidation proceeds at relatively low temperatures. So, a locally oxidized Cu line is an n-p-n structure. A gate effect in such structures has been demonstrated. Moreover, the Cu₂O films obtained by oxidation of vacuum evaporated Cu layers were characterized with various spectroscopic methods (X-ray diffraction, FTIR, and spectroscopic ellipsometry I). *Fig. 1.4.4* shows transistors based on Cu₂O and *fig. 1.4.5* shows typical I-V characteristics of these transistors. These transistors were stable with time.



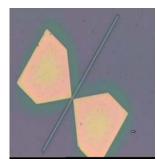
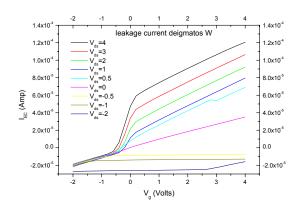


Fig. 1.4.4: $Cu-Cu_2O-Cu$ transistors formed by oxidizing the central part of a Cu structure shown in the photos. The whole configuration was covered by a photoresist on which a trench was formed to allow for the oxidation of the uncovered Cu film.



*Fig. 1.4.5: Typical I-V characteristics taken on Cu-Cu*₂*O-Cu transistors.*

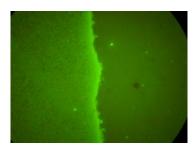
d) Smart materials

V. Vamvakas, V. Assimakopoulos, Y. Aspiotis and D. Pappas (with the contribution of M. Vassilopoulou in device fabrication)

 WO_3 films may be doped reversibly when in contact with an electrolyte and under an electric field. This reversible doping implies significant changes in their optical and electrical properties, which can be used in applications such as in displays and in gas sensors.

 WO_3 -based displays have been shown in the past. The reversible changes of color in WO_3 films are accompanied with reversible changes of their electric resistance. Therefore, these films may be used for the fabrication of resistive gas sensors. The integration of a display and a gas sensor, both based on the same WO_3 film on the same substrate is under development.

 WO_3 films may also be used for the stabilization of proteins which depends on the doping of WO_3 films. In *fig. 1.4.6* the adsorption of RgG, assayed with fluorescein-labeled antirabbit IgG antibody, on colored (left) and bleached (right) WO_3 strips using fluorescence microscopy is shown. It can be seen that the proteins are preferentially stabilized on the bleached material. The stabilization of proteins on WO_3 , except of doping, also depends on pH as shown in *fig. 1.4.7*.



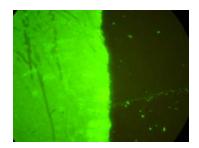


Fig. 1.4.6: Adsorption of RgG on colored (**left**) and bleached (**right**) WO_3 strips. For the colored strips the photoluminescence intensity is almost equal on the strip and on the glass substrate (**left photo**). The photoluminescence intensity on the bleached strips is much higher than on the glass (**right photo**).

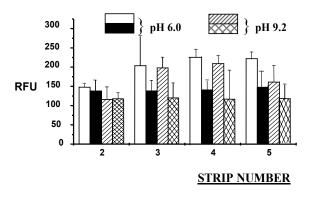


Fig. 1.4.7. Photoluminescence density measured at two different pHs on a colored (doped) (2), two uncoloured (3, 4) and a colored and bleached (5) strip. The error bars were obtained from many measurements taken at various locations on each photograph.

Within the same activity silicones used in a variety of applications ranging from the encapsulation of solar cells to micro-systems are under investigation. Applications in the above fields are under development.

Publications in International Journals

- 1. Comparison of FTIR transmission spectra of thermally and LPCVD grown by TEOS pyrolysis, SiO₂ films V. Em. Vamvakas and D. Davazoglou. *Journal of the Electrochemical Society* Vol. 151, 93 (2004)
- "Fabrication of very fine copper lines on silicon substrates patterned with PMMA via selective chemical vapor deposition" D. Davazoglou, I Raptis, A. Gleizes and M. Vassilopoulou, Journal of Vacuum Science and Technology B Vol. 22, 859 (2004)
- 3. "Optical properties of SiO₂-TiO₂ sol-gel thin films" P. Chrysicopoulou, D. Davazoglou, C. Trapalis and G. Kordas *Journal of Materials Science* 39 (8): 2835-2839 (2004)

PROGRAM II

NANOSTRUCTURES and NANOELECTRONIC DEVICES

Project II. 1: SEMICONDUCTOR NANOSTRUCTURES: SCIENCE & APPLICATIONS

Project leader: Dr A. G. Nassiopoulou

Other key researchers: V. Ioannou-Sougleridis, E. Tsoi, P. Normand and N. Papanikolaou Phd students: M. Kokonou, A. Olziersky, A. Salonidou, A. Zoy

Projects Running:

- EU IST FORUM FIB, Contract Nº: 29573
- EU IST FET ESCHER, Contract Nº: 33287
- EU NoE IST SINANO, Contract Nº: 506844

Main objectives:

- Fabrication and characterization of semiconductor nanostructures (quantum wires, quantum dots, optical properties, charging effects, self-assembling, ordering)
- Application in non-volatile memories
- Self-assembled building blocks for nanoelectronics (self-assembly of nanoparticles, ordering on microcrystals, application in nanoelectronic devices, transport properties)
- Calculation of heat transport in the nanoscale with molecular dinamics

Mail results in 2004:

a) Two-demensional arrays of ordered, highly dense and ultra small Ge nanocrystals in thin SiO₂ layers

A. Olzierski, E. Tsoi and A. G. Nassiopoulou

In this work, we have developed, in collaboration with ISI/FZJ Julich and CRMC₂-CNRS-Marseille, two original processes for the fabrication of 2-dimensional arrays of ordered Ge nanocrystals embedded in thin SiO₂ layers for their use in nanocrystal floating gate memories. Ordering is achieved by a combination of focused ion beam nano-patterning and self assembly of Ge islands on the patterned SiO₂ surface. In the first process the Ge islands are grown by selective chemical vapor deposition of Si / Ge / Si on Si holes fabricated by FIB patterning, while the second process uses solid phase epitaxy by MBE of amorphous Ge on SiO₂ at room temperature, followed by annealing for crystallization. Highly ordered and highly dense $(1.5 \times 10^{11}/\text{cm}^2)$ ultra-small (~ 20 nm) Ge dots on SiO₂ were achieved by both processes. Examples are given *in fig. II.1.1* This work has been carried out within the European IST project FORUM FIB: Fabrication, Organisation and Use of Memories obtained by Focused Ion Beam.

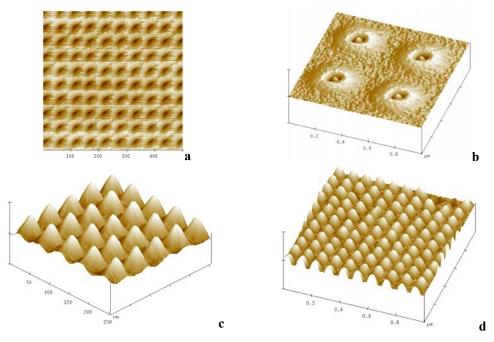


Fig. II.1.1: AFM images of a regular array of FIB holes with diameter of about 40 nm before (a) and after (b) the deposition of Si/Ge/Si stack. (c) and (d) show the perfectly uniform 2D dot arrays after oxide removal in an area of $250 \times 250 \text{ nm}^2$ and $1 \times 1 \text{ µm}^2$ respectively.

b) 2-D Silicon nanocrystal layers within SiO₂ by LPCVD deposition of amorphous silicon, followed by solid phase crystallization and thermal oxidation.

E. Tsoi, A. Salonidou, V. Ioannou-Sougleridis, P. Normand, and A. G. Nassiopoulou

Silicon nanocrystals memory cells of an n-MOSFET type were fabricated and tested, based on a silicon nanocrystal gate MOS structure fabricated by low-pressure chemical vapor deposition (LPCVD) of amorphous silicon (α -Si) on a tunneling silicon dioxide layer, followed by solid phase crystallization and high temperature thermal oxidation. A layer of silicon nanocrystals embedded in SiO₂ at a tunneling distance (3.5nm) from the silicon substrate was thus formed. The obtained memory cells showed a full-write, full-erase memory window of the order of 0.5V under charging with pulses of 7V and -8V respectively at 100 ms.

The influence of oxide traps (located near the Si substrate-tunnel oxide interface) on the charging characteristics of Si-nanocrystals embedded within SiO_2 layers were investigated by monitoring the admittance characteristics at room temperature. In the samples investigated, an oxide hole trap located almost at the Si-SiO₂ interface of the silicon substrate, having a distribution of energy states, has been detected, which controls the hole injection and transfer to the Si nanocrystals. Upon capturing a hole the defect energy levels undergo a transition due to lattice relaxation effects and hole charging of the Si-nanocrystals occurs via an inelastic two-step tunneling mechanism. High temperature annealing was found to reduce the density of these near-interfacial defects, therefore reducing the coupling between the Si-nanocrystals and the substrate.

c) Very thin porous alumina films on silicon for use as templates for nanofabrication

M. Kokonou and A. G. Nassiopoulou

By anodizing thin aluminum films on Si in sulfuric or oxalic acid aqueous solutions, we get anodic alumina films with ordered cylindrical vertical pores, arranged in a hexagonal close-packed structure. The diameter of the pores is in the range of 10 to 100 nm, depending on the electrochemical solution used.

In this work, very thin anodic alumina films were fabricated, with thickness down to ~ 10 nm. These films may be used as templates for the fabrication of arrays of quantum wires or dots for use in nanoelectronic devices.

By monitoring the anodization time it is possible to fabricate ordered SiO_2 nanodots at the bottom of each vertical pore (at the interface of alumina with silicon). By dissolving the alumina film, a 2-D array of SiO_2 nanodots is obtained. This patterned $Si-SiO_2$ surface is very appropriate for the growth of ordered 2-D arrays of silicon nanocrystals.

Fig. II.1.2 shows AFM images of SiO₂ nanodots on silicon, fabricated through an alumina template.

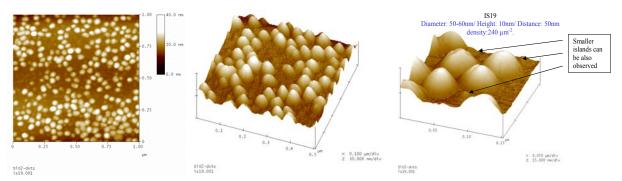


Fig. II.1.2: AFM images of SiO₂ nanodots on silicon, fabricated through an alumina template.

d) Self-organized building blocks for nanoelectronic devices.

A. Zoy, V.Ioannou-Sougleridis and A. G. Nassiopoulou

This activity was carried out within the IST ESCHER project (EU Framework program). The main objective was to fabricate self-assembled building blocks for nanoelectronics, using the crystal-latticemediated self-assembly process (CLAMS, proprietary process of one of the partners-Strathclyde University). Nanoparticles are self-assembled on microcrystals in a solution by the above technique, which are then selforganized on an oxidized silicon substrate between electrodes by either structural modification of the Si surface between the electrodes or by using field-assisted deposition. The nanoparticles used so far were composed of Au or ZnS and microcrystals were composed of K_2SO_4 .

Fig. II.1.3 (a) below shows a block of Au-nanoparticles on K_2SO_4 microcystals. Nanoparticles are composed of a Au nucleus surrounded by tiopronin. *Fig. II.1.3* (b) shows Au nanoparticle-coated K_2SO_4 microcrystals deposited between Au electrodes by selective field-assisted deposition

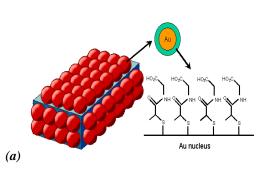


Fig. II.1.3 (a): Au nanoparticles self-assembled on K_2SO_4 microcrystal. Nanoparticles are composed of a Au nucleus surrounded by tiopronin.

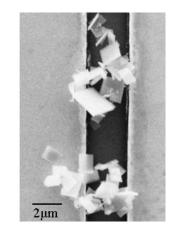


Fig. II.1.3 (b): SEM image of Au nanoparticlescoated K_2SO_4 microcrystals deposited between Au electrodes by electric-field-assisted deposition.

e) Heat transport simulations in the nanoscale with molecular dynamics.

N. Papanikolaou

Thermal properties on the nanoscale are becoming an important issue as the size of the electronic elements decreases. Our aim is to study the thermal properties of semiconductor materials using molecular dynamics. A classical molecular dynamics simulation program is currently under development. The program is designed to be general enough to handle different materials as well as to be able to simulate effects like crystallization or growth. We intent to apply molecular dynamics methods to study thermal transport properties in order to elucidate effects like interfacial thermal resistance or modification of the thermal properties in nanostructures like multilayers or dot arrays. The hope is to eventually use computer simulations to design material with tailored thermal properties.

(b)

PUBLICATIONS in INTERNATIONAL JOURNALS

- "Silicon nanocrystals in SiO₂ thin layers", Nassiopoulou A. G., *Encyclopedia of Nanoscience and Nanotechnology*, edited by H. S. Nalwa, vol. 9 p. 793-813 (2004)
- "Selective self-alignment of Au nanoparticle-coated K₂SO₄ microcrystals in micrometer gratings of V-grooves on a silicon substrate", Nassiopoulou A. G., Zoy A., Ioannou-Sougleridis V., Olzierski A., Travlos A., Martinez-Albertos J. L. and Moore B., *Nanotechnology* 15, 1-5, 352-356, (2004)
- 3. "Growth of two-dimensional arrays of silicon nanocrystals in thin SiO₂ layers by low pressure chemical vapour deposition and high temperature annealing/oxidation. Investigation of their charging properties", Salonidou A., Nassiopoulou A. G., Travlos A., Ioannou-Sougleridis V. and Tsoi E., *Nanotechnology* 15, 1-7, 1233-1239, (2004)
- 4. "Transient and ac electrical transport under forward and reverse bias conditions in aluminium/ porous silicon/p-cSi structures", Theodoropoulou M., Karahaliou P. K., Krontiras C. A., Georga S. N., Xanthopoulos N., Tsamis C. and Nassiopoulou A. G., *J. Appl. Phys.* 96, 12, (2004)
- 5. "Influence of magnetic field on electromagnetic instabilities in Semiconductor superlattices", Tarkhanyan R. H. and Nassiopoulou A. G., *J. Nanosci. Nanotech.* 4, 1085, (2004)
- "Two-dimensional arrays of nanometer scale holes and nano-V-grooves in oxidized Si wafers for the selective growth of Ge dots or Ge/Si hetero-nanocrystals", Olzierski A., Nassiopoulou A. G., Raptis I. and Stoica T., *Nanotechnology* 15, 1695-1700 (2004)
- 7. "Transient and ac conductivity of nanocrystalline porous alumina thin films on silicon, with embedded silicon nanocrystals" J. of Applied Physics, 95,5, 2776-2780 (2004)

PRESENTATIONS in CONFERENCES

- 1. "FORUM FIB: Fabrication organization and use of memories obtained by Focused Ion Beam", I. Berbezier, A. Karmous, A. Ronda, T. Stoica, R. Geurt and A.G. Nassiopoulou, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- "Ultrafast carrier dynamics in highly implanted and annealed polycrystalline silicon films", E. Lioudakis, A. Othonos and A.G. Nassiopoulou, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- 3. "Nanotemplate alumina films on a silicon substrate fabricated by electrochemistry", M.Kokonou, A. G. Nassiopoulou, K. P. Giannakopoulos and N. Boukos, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- 4. "Generation of guided terahertz electromagnetic waves in semiconductor superlattices", R.H.Tarkhanyan and A.G. Nassiopoulou, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- "Investigation of electronic conductivity of nanoparticle coated microcrystals", A. Zoy, A. G. Nassiopoulou, M. Murugesan and B. Moore, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece (to appear in J. of Phys. Conf. Series)
- 6. "Influence of near interface oxide traps on the charging characteristics of Si nanocrystals embedded within SiO₂", V. Ioannou-Sougleridis and A. G. Nassiopoulou, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- "Silicon nanocrystal memory cells by low pressure chemical vapor deposition of amorphous silicon on SiO₂ and oxidation", E. Tsoi, P.Normand, A.G. Nassiopoulou, V. Ioannou-Sougleridis and A. Salonidou, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- "Density of interface traps in ultra thin porous anodic alumina films on silicon", M. Theodoropoulou, P.K. Karahaliou, S.N. Georga, C.A. Krontiras, M.N. Pisanias, M. Kokonou and A.G. Nassiopoulou, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- 9. "Ordered 2-D arrays of Ge quantum dots embedded in ultra thin SiO₂", A. Olzierski, A. G. Nassiopoulou and A. Travlos, *EMRS 2004*, Strasbourg, France
- "Very thin anodic alumina films with ordered pore arrays on a silicon substrate", M. Kokonou, A. G. Nassiopoulou and K. P. Giannakopoulos, *International Conference on Porous Semiconductor Science and Technology*, Valencia, Spain, March 14-19, 2004
- 11. "Photoluminescence of very thin anodic alumina films on a silicon substrate", M. Kokonou and A. G. Nassiopoulou, International Conference on Porous Semiconductor Science and Technology, Valencia, Spain, March 14-19, 2004
- 12. "2-D arrays of Ge quantum dots in SiO₂ for non-volatile memories", A. Olzierski, A. Nassiopoulou, A. Travlos, T. Stoica, *XX Panhellinion Conference on Solid State Physics and Materials Science26-29 September*, Ioannina 2004
- 13. "Porous alumina thin films on Si with self-assembled vertical pores", M. Kokonou, A. G. Nassiopoulou and K. P. Giannakopoulos, XX Panhellinion Conference on Solid State Physics and Materials Science26-29 September, Ioannina 2004
- "Study of interface state density in porous alumina/c-Si MOS structures", M. Theodoropoulou, P. Karachaliou, S. N. Georga, C. Krontiras, M. Pizanias, M. Kokonou and A. G. Nassiopoulou, XX Panhellinion Conference on Solid State Physics and Materials Science26-29 September, Ioannina 2004

INVITED TALKS

1. "Low dimensional Si or Ge for application in nanodevices", A. G. Nassiopoulou, **Invited talk**, *International Workshop on ultimate Lithography and Nanodevice Engineering*, Agelonde, France, 13-16 June 2004

- 2. "2-D arrays of Semiconductor nanocrystals in thin SiO₂ layers application in quantum dot memories", A. G. Nassiopoulou, **Invited talk**, *E-MRS spring Meeting Symposium I*, May 24-28, 2004
- 3. "Low-dimensional Si for optoelectronics and memory devices, A. G. Nassiopoulou, **Invited talk**, *NATO Advanced Study Institute on Nanostructured and Advanced Materials for Optoelectronic, Photovoltaic & Sensor applications*, Sozopol, Bulgaria, September 6-17, 2004

PROGRAM II

NANOSTRUCTURES and NANOELECTRONIC DEVICES

Project II. 2: SILICON NANOCRYSTAL MEMORIES

Project leader: P. Normand

Other key researchers (From the Institute): C. Tsamis Post-doctoral: D. Skarlatos, V. Vamvakas PhD candidates: E. Kapetanakis, P. Dimitrakis, S. Koliopoulou External collaborators: D. Tsoukalas (NTUA)

Projects Running:

- EC GROWTH GRD1-2000 -Nanocrystals for electronic applications, NEON- Nº25619

<u>Goals :</u>

- To explore and develop novel technological routes for generating nanocrystal based structures aiming at electronic memory applications.

- To fabricate, evaluate and optimize nanocrystal memory devices for low-voltage high-density data storage.

- To transfer laboratory nanocrystal memory technology to industry.

Main results:

a) Silicon nanocrystal memory devices obtained by low-energy ion-beam-synthesis

Nonvolatile memory technology using discrete charge storage nodes embedded in the gate oxide of metal-oxide-semiconductor (MOS) devices offers an attractive alternative for extending the scaling of conventional floating-gate memories. Among the various processing routes explored during the last few years for generating such storage nodes in the form of nanocrystals (NCs), the ion-beam-synthesis (IBS) technique has received substantial attention due to its flexibility and manufacturing advantages. The potential of IBS for NC-based memories operating at low voltages has been recently enhanced through the synthesis in the low-energy (LE) regime (typically 1keV) of single Si-NC layers in thin SiO₂ films. Thanks to NEON European framework, the LE-IBS technique surpassed the level of 'proof of concept' and promising devices for true nonvolatile memory applications have been recently achieved at IMEL (Dimitrakis et al. SSE 2004). In addition to the numerous materials and electrical studies developed for understanding and manipulating the formation of Si NCs by LE-IBS (Bonafos et al. JAP 2004), major efforts have been devoted to identify and solve fabrication issues encountered during the integration of this technique in a manufacturing environment (Normand et al. NIMB 2004).

Prototype nanocrystal memory devices were recently fabricated at STMicroelectronics on 8-inch wafers using a conventional process flow based on a 0.15μ m Flash-EEPROM technology. The devices were isolated following a shallow-trench-isolation (STI) procedure. N-MOSFETs memory cells with gate lengths and widths ranging from 0.16 to 10 μ m have been achieved. Taking into account electrical investigations conducted at STM and IMEL, it was concluded that these devices suffer from high boron contamination that leads to large threshold voltage shifts and variations across the wafers. Despite this cross-contamination effect that occurs during Si implantation, small fluctuations in memory windows under P/E operation were observed in the case of large-channel transistors. This result is important since it suggests that the LE-IBS process was quite uniform over the wafers.

Most important of all, our investigations showed that parasitic transistors (FET_P) affect drastically the device performance. The action of FET_P that can be detected through a "subthreshold hump" in the transfer characteristics of the MOSFETs leads to a substantial degradation of the electrical properties of the intended devices and dominates the memory behavior of deep submicronic cells. This detrimental effect goes maybe beyond the LE-IBS-related-concerns and could constitute a technological issue towards the integration of NC floating-gate in conventional memory architecture (see Dimitrakis and Normand MRS Fall Meeting 2004).

b) Memory devices obtained by Si⁺ irradiation through poly-Si/SiO₂ gate stack

As already emphasized the LE-IBS technique leads to promising device results and many fabrication issues have been identified and solved for its integration at an industrial level. However, while ion implantation into uncapped gate oxides offers a number of processing alternatives for damage recovery, removal of near surface atoms (sputtering effect) during implantation and oxide contamination (e.g. from ambient moisture) between the implantation and annealing steps cannot be avoided. To be efficient, the alternative of using a protecting layer (e.g. poly-silicon) deposited onto the gate oxide before ion implantation would require high-energy implants and thus, the advantages of the LE-IBS technique will be rapidly lost.

In an effort to overcome this concern, NEON Partners from Research Center Rossendorf have recently proposed a different approach using Si ion irradiation through a poly-Si/SiO₂ gate stack. Fabrication of memory devices exploiting the above technique has been successfully achieved at ZMD (Zentrum Mikroelektronik Dresden AG) on 6 inch wafers using 0.6 µm CMOS technology rules. These devices were tested by ZMD and IMEL. The charge storage characteristics of these devices for different process conditions (Si irradiation fluence, thermal budget) have been examined in terms of memory windows for different programming/erasing times and voltages. Endurance to successive program/erase cycles and retention time characteristics up to 125°C of selected devices have been also tested. Low-voltage and high-speed operating memory cells that can endure 10⁷ programming/erasing cycles have been demonstrated. While excellent device uniformity and reproducibility have been observed over the wafers, data retention evaluation reveals that more research is still required to fine tune the fabrication process and insure a 10-year memory window for nonvolatile memory applications (see Dimitrakis et al. MMN 2004 Conference).

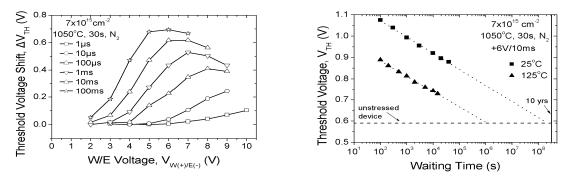


Fig. II.2.2: Single-MOSFET memory cell obtained by Si ion irradiation through the poly-Si/SiO₂ gate stack. *Left:* Memory windows obtained by sequential W/E pulses with different heights and widths. *Right:* Charge retention characteristics at room temperature (*RT*) and 125 °C.

c) Ge nanocrystals in MOS-memory structures produced by molecular-beam epitaxy and rapid-thermal processing

Our team was here in charge of the electrical characterization of SiO₂ layers with embedded Ge nanocrystals obtained by a molecular beam epitaxy (MBE) based process developed at the University of Aarhus (DK) within NEON framework. This process allows the generation of a sheet of crystalline Ge nanodots at any wanted depth in the oxide. Production of an area-dot density of 5x10¹¹ cm⁻² of crystalline Ge dots of 4 nm in diameter located in the silicon oxide at 3-4 nm from the Si/SiO₂ interface has been demonstrated. Charge storage behavior of these structures has been investigated through C-V and I-V measurements of Al gate capacitors (*see Kanjilal et al., Appl. Phys. A 2004*). Memory windows of about 0.2 and 0.5 V for gate voltage round sweeps of 3 and 6 V, respectively, corresponding to electric fields around 2.22 and 4.44 MV/cm have been achieved. The density of interface states at mid-gap evaluated through quasistatic and high-frequency C-V measurements is on the order of 10¹¹ eV⁻¹cm⁻². Although further investigations in terms of charge retention time and write/erase pulsed operation are required to definitively conclude on the memory behaviour of oxides with embedded MBE-formed Ge nanocrystals, the above results indicate that the MBE method is well-suited for the further development of nanocrystal floating gate memory cells.

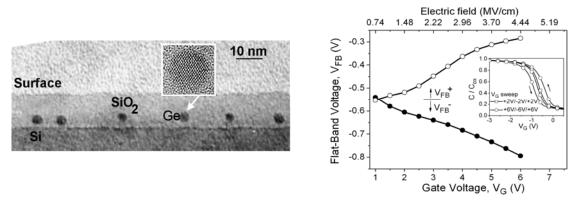


Fig. II.2.3: Left: Bright field TEM image of a cross-section sample with a 0.7 nm thick Ge layer after oxidation at 800°C for 14 min followed by reduction at 950 °C for 30 in N_2 . Insert: high-resolution TEM picture of a Ge nanocrystal. **Right:** Flat-band voltage vs gate voltage (V_G) characteristics for different $+V_G/-V_G/+V_G$ sweep sequences of a 14nm-thick oxide layer with embedded Ge nanocrystals.

d) Hybrid silicon-organic memory devices using gold nanoparticles

This research aims at the exploration of an inexpensive technology that combines silicon nanofabrication techniques and the emerging area of intra-molecular electronics to develop high-density memory arrays. This activity is conducted in close collaboration with the University of Durham and was initiated within the framework of the IST-FET European project Fracture (2001-2003). Last year, our research activities have been concentrated on the fabrication of hybrid memory nanoparticle FET devices using conventional silicon process steps integrated with chemical processing for nanoparticle deposition and Langmuir-Blodget deposition technique for organic insulator deposition (control insulator). These films were deposited on top of a thermal oxide that makes the interface with the silicon channel (tunnelling oxide). The devices exhibit non-volatile memory characteristics and remain stable at room temperature for an investigated retention time of 6 months.

This year, we demonstrated MISFET memory devices that incorporate a monolayer of Langmuir-Blodgett (LB)-deposited-gold nanoparticles as floating-gate charge storage elements (Kolliopoulou et al. MRS Fall Meeting 2004). The devices were fabricated on a SOI substrate using conventional silicon processing. The nanoparticle layer was separated from the channel area of the FET with a 5 nm thermal SiO₂ layer and isolated from Al gate contact with a LB-deposited organic (Cadmium Arachidate, CA) insulator layer. The memory behavior of the devices was evaluated under pulsed gate-voltage operation conditions. While significant nanocrystal charging from the channel is detected at low voltage pulses (< 5 V), charge injection from the gate occurs for higher voltages due to the poor insulating properties of the CA layer. Replacement of the later with a less conductive material is underway for device performance improvement.

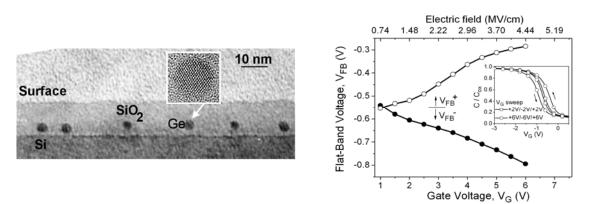


Fig. II.2.3: Left: Bright field TEM image of a cross-section sample with a 0.7 nm thick Ge layer after oxidation at 800°C for 14 min followed by reduction at 950 °C for 30 in N_2 . Insert: high-resolution TEM picture of a Ge nanocrystal. **Right:** Flat-band voltage vs gate voltage (V_G) characteristics for different $+V_G/+V_G/+V_G$ sweep sequences of a 14nm-thick oxide layer with embedded Ge nanocrystals.

PUBLICATIONS in INTERNATIONAL JOURNALS

- "Nanocrystals manufacturing by ultra-low-energy ion-beam-synthesis for nonvolatile memory applications", P. Normand, E. Kapetanakis, P. Dimitrakis, D. Skarlatos, K. Beltsios, D. Tsoukalas, C. Bonafos, G. Ben Asssayag, N. Cherkashin, A. Claverie, J. A. Van Den Berg, V. Soncini, A. Agarwal, M. Ameen, M. Perego, M. Fanciulli, *Nucl. Instr. Meth. Phys. Res. B (NIMB)* 216, 228-238 (2004)
- "Silicon nanocrystal memory devices obtained by ultra-low-energy ion-beam-synthesis", P. Dimitrakis, E. Kapetanakis, D. Tsoukalas, D. Skarlatos, C. Bonafos, G. Ben Asssayag, A. Claverie, M. Perego, M. Fanciulli, V. Soncini, R. Sotgiu, A. Agarwal, M. Ameen, P. Normand, *Solid State Electronics* 48, 1511-1517 (2004)
- "Manipulation of two-dimensional arrays of Si nanocrystals embedded in thin SiO₂ layers by low energy ion implantation", C. Bonafos, M. Carrada, N. Cherkashin, H. Coffin, D. Chassaing, G. Ben Assayag, A. Claverie, T. Muller and K. H. Heinig, M. Perego and M. Fanciulli, P. Dimitrakis, P. Normand, J. Appl. Phys. 95, 5696-5702 (2004)
- 4. "Size and aerial density distributions of Ge nanocrystals in a SiO₂ layer produced by molecular beam epitaxy and rapid thermal processing", A. Kanjilal, J. Lundsgaard Hansen, P. Gaiduk, A. Nylandsted Larsen, P. Normand, P. Dimitrakis, D. Tsoukalas, N. Cherkashin, A. Claverie, *Appl. Phys. A Mater. Sc. Process. Online* (June 2004)
- "Processing issues in silicon nanocrystal manufacturing by ultra-low-energy ion-beam-synthesis for non-volatile memory applications", P. Normand, P. Dimitrakis, E. Kapetanakis, D. Skarlatos, K. Beltsios, D. Tsoukalas, C. Bonafos, H. Coffin, G. Benassayag, A. Claverie, V. Soncini, A. Agarwal, Ch. Sohl, M. Ameen, *Microelectronic Engineering* 73-74, 730-735 (2004)
- "Integration of organic insulator and self-assembled gold nanoparticles on Si MOSFET for non-volatile memory cells", S. Kolliopoulou, P. Dimitrakis, P. Normand, H-L. Zhang, N. Cant, S. D. Evans, S. Paul, C. Pearson, A. Molloy, M. C. Petty, D. Tsoukalas, Microelectronic Engineering 73-74, 725-729 (2004)

PRESENTATION IN CONFERENCES

- "Memory devices obtained by Si⁺ irradiation through poly-Si/SiO₂ gate stack", P. Dimitrakis, P. Normand, E. Votintseva, K-H. Stegemann, K-H. Heinig, B. Schmidt, Oral presentation, International Conference on Microelectronics Microsystems Nanotechnology, MMN 2004, Athens, Greece, November 14-17 (2004)
- "Field effect devices with metal nanoparticles integrated by Langmuir-Blodgett technique for non-volatile memory applications", S. Kolliopoulou, D. Tsoukalas, P.Dimitrakis, P. Normand, S. Paul, C. Pearson, A. Molloy, M. C. Petty, Poster presentation, *International Conference on Microelectronics Microsystems Nanotechnology, MMN04*, Athens, Greece, November 14-17 (2004)

INTERNATIONAL CONFERENCE PROCEEDINGS

- "Manipulation of 2D-Arrays of Si Nanocrystals Embedded in a Thin SiO₂ Layer by Low Energy Implantation", C. Bonafos, G. Ben Assayag, S. Schamm, H. Coffin, N. Cherkashin, A. Claverie, P. Normand, P. Dimitrakis, M. Perego, M. Fanciulli, T. Mueller, K-H. Heinig, M. Tence, C. Colliex, **Oral presentation**, *Materials Research Society Fall Meeting 2004, MRS Fall 04*, Symposium D, Boston, USA, November 29 December 3 (2004)
- "Ge Nanocrystals in MOS-Memory Structures Produced by Molecular-Beam Epitaxy and Rapid-Thermal Processing", A. Nylandsted Larsen, A. Kanjilal, J. L. Hansen, P. Gaiduk, P. Normand, P. Dimitrakis, D. Tsoukalas, N. Cherkashin, A. Claverie, **Poster presentation**, *Materials Research Society Fall Meeting 2004, MRS Fall 04, Symposium D*, Boston, USA, November 29 - December 3 (2004)
- "Oxidation of Si nanocrystals obtained by low energy ion implantation in a thin SiO₂ layer", H. Coffin, C. Bonafos, N. Cherkashin, S. Schamm, G. Ben Assayag, G. Zanchi, P. Dimitrakis, P. Normand, M. Tence, C. Colliex, A. Claverie, **Poster presentation**, *Materials Research Society Fall Meeting 2004, MRS Fall 04, Symposium D*, Boston, USA, November 29 - December 3 (2004)
- 4. "Gold Langmuir-Blodgett deposited nanoparticles for non-volatile memories", P. Dimitrakis, S. Kolliopoulou, D. Tsoukalas, P. Normand, S. Paul, C. Pearson, A. Molloy, M. C. Petty, **Poster presentation**, *Materials Research Society Fall Meeting 2004, MRS Fall 04, Symposium D*, Boston, USA, November 29 December 3 (2004)
- "A Si/SiGe MOSFET utilizing low-temperature wafer bonding", S. Kolliopoulou, P. Dimitrakis, D. Goustouridis, S. Chatzandroulis, P. Normand, D. Tsoukalas, H. Radamson, Poster presentation, International Conference on Micro-and Nano-Engineering, MNE04, Rotterdam, Netherlands, September 19-22 (2004)
- 6. "Single electron charging mechanisms into silicon quantum dots realized by ultra low energy implantation", **Oral presentation**, A. Beaumont, P. Normand, G. Ben Assayag, A. Claverie, A. Souifi, *European Materials Research Society Conference, E-MRS04*, Strasbourg, France, June (2004)

INVITED TALKS

- 1. "Semiconductor nanocrystal floating-gate memory devices", P. Dimitrakis and P. Normand, **Invited talk**, *Materials Research Society Fall Meeting 2004, MRS Fall 04, Symposium D*, Boston, USA, November 29 December 3 (2004)
- 2. "Nanocrystal memory for future electronics", P. Normand, **Invited talk**, 13th European Workshop on *Heterostructure Technology, HETECH 2004*, Heraklion, Greece, October 3-6 (2004)

PROGRAM II

NANOSTRUCTURES and NANOELECTRONIC DEVICES

Project II.3:MOLECULAR MATERIALS as COMPONENTS of ELECTRONIC DEVICES

Project leader: N. Glezos

Other key researchers: P. Argitis, V. Ioannou-Sougleridis PhD candidates: D. Velesiotis, G. Chaidogiannos

Projects Running:

- Greek Czech Cooperation project (GSRT)
- EU RTD project Uninanocups

<u>Goals</u>

- To investigate the potential of molecular materials in the class of polyoxometalates to be used as active components in molecular devices e.g. as switching or memory elements.
- To evaluate elements of the class of metal phthalocyanines as components of organic FETs
- To investigate electronic transport in the atomic limit

Main results:

a) Molecular nanodevices containing polyoxometalates

D. Velessiotis, N.Glezos, V. Ioannou-Sougleridis and G. Chaidogiannos

Molecular materials are being extensively investigated as components of electronic devices hoping to deminish device dimensions to the atomic scale. Polyoxometalates (POMs) are a class of welldefined metal oxygen clusters that can be envisioned as soluble molecular semiconductors. These compounds for reasons of cationic radius size and oxygen $p\pi$ bonding capabilities can be formed having as basis only 5 elements of the periodic table (V, Nb, Ta, Mo, W) but the most stable and well characterized elements that offer substantial

chemical handling capability and property tunability are those based on WO_4^{2-} and MOO_4^{2-} , primarily $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_3SiMo_{12}O_{40}$ and $H_3SiW_{12}O_{40}$.

The work of this group on tungstate POMs has been motivated by the comparison of the electronic properties of these molecules to metallic and conducting nanoclusters. POMs are stable inorganic oxides of size ~1nm that do not suffer from the limitations of size and process reproducibility. Their charging energies are in the range of 0.1-4.0 eV therefore the resolution of discrete electronic levels at room temperature conditions is expected. The search for a suitable polymer matrix resulted in poly (methyl methacrylate) PMMA, although other systems have also been tested. The host material should not react with the embedded molecules, thus altering their transport properties, and at the same time the composite material should preferably behave as a lithographic resist with nanometer resolution for nanofabriation process simplification reasons. PMMA meets both demands. The electrical transport properties of polymer/POM blends were tested using planar and vertical devices with nanometer distant electrodes. Aluminum or gold planar electrodes distant 20-500nm apart were fabricated on silicon dioxide using a standard PMMA lift-off process and electron beam lithography. Two different electrode configurations have been used a) in the shape of opposing fingers with a nanometer distance and b) in the shape of parallel lines with nanometer interspacing.

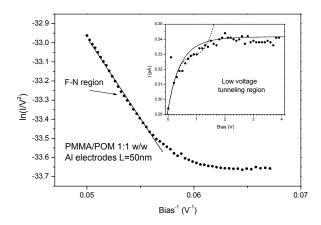


Fig. II.3.1: Analysis of the tunneling regimes in the case of a 50nm Al contact. The low voltage region is shown in the inset. The experimental curve is fitted using both the low power extrapolation model and the model of Simmons.

In order to study the transport characteristics and single out the tunneling effects of these composite systems, the electrode distance, the electrode material and the molecular concentration were treated as variable parameters. In the case of inter-electrode distances larger than 50 nm the behavior is approximately Ohmic with the exception of a small non linear region for voltages lower than 1V. This Ohmic behaviour is due to hopping conductivity through tungstate molecules which in our case are distant 2.25nm apart. Since the molecular size is 1-1.5 nm the net distance between molecules is estimated to be 0.75-1.25nm in this concentration. In the case of small interelectrode distance for L=50nm, a nonlinear plateau appears. The plateau suggests a saturation effect i.e. the transition from the barrier limited conduction to the bulk limited conduction dominated by hoping transport. In order to investigate this effect and distinguish the part that is due to the insulating PMMA matrix, structures with Au electrodes were also tested. The conductivity plateau still appears and this is evidence of the fact that it is mainly dependent on the material, rather than the electrode. Comparing the results in the case of Al and Au electrodes it is deduced that the barrier appears for smaller electrode distances in both cases. Effects are less dramatic in the case of Al electrodes due to the presence of the natural oxide which has a high contribution in the case of lower voltages. We have checked electrode distances as low as 10nm obtaining qualitatively the same results. In the case of such small distances only a few molecules are aligned in the direction of the electric field. For example, in the case of a 1:1 w/w concentration and 10 nm electrode distance, the mean distance between molecules is <d>=3nm resulting in 3-4 molecules along the field. The electrons reach the molecules through the PMMA insulating barrier undergoing multiple tunneling.

b) Evaluation of sulfonated metal phthalocyanines for OTFT applications

G.Chaidogiannos, N.Glezos, K.Yannakopoulou¹, I.M.Mavridi¹, S. Kennou², F. Petraki² and S. Nespurek³

¹Institute of Physical Chemistry, NCSR "Demokritos"

²Department of Chemical Engineering, University of Patras, 26504 Rion, Patras, Greece

³Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06, Prague 6, Czech Republic

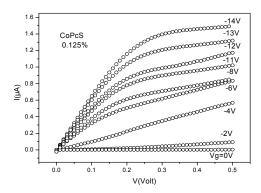
Organic thin film transistors (OTFTs) have already been used in diverse applications such as electronic paper, chemical sensors, radio frequency tags and memory devices. Pentacene and α -sexithiophene are the molecular materials with the highest reported field mobilities as p-channels in OTFTs. However both materials present processing difficulties due to their limited solubility. Metal phthalocyanines (MePc) is another class of compounds which has been investigated for the same purpose. Their advantages are their chemical and thermal stability (stable up to 400°C, easily vacuum evaporated). Their field mobilities in transistor structures are of order 0.01 cm²/V.s (for CuPc).

We investigate the class of metal phthalocyanine sulfonate sodium salts (MePcS_x) as candidates for ptype channels in organic transistors. These materials were selected because of their enhanced solubility compared to their unsulfonated counterparts. Sulfonated MePcs have been either synthesized (Me = Co or Zn, Cobalt or Zinc phthalocyanine; mixtures of monosulfo and disulfo derivatives), or purchased from Aldrich Co (Me=Cu, Copper phthalocyanine-3, 4', 4", 4"'-tetrasulfonic acid tetrasodium salt, 85% dye content). CoPcS₁₋₂ and ZnPcS₁₋₂ were prepared from Co or Zn phthalocyanine, respectively, dissolved in 10 % fuming sulphuric acid and subsequently heated (85°C, 6 h). The reaction mixture was pured into the mixture of water and ice, filtered and washed. The filter cake was dispersed in water and pH adjusted with NaOH to the value of about 11. Metal phthalocyaninesulfonate was changed into dark blue water soluble sodium salt, which was isolated by evaporation of water by using a water bath. Preliminary tests for Al (OH) PcS_x based transistors have given promising results.

Both spin coating and vacuum evaporation are used for the film preparation. After the spin coating, the samples are sequentially stored in room temperature for 4 h., dried in vacuum (0,1 atm) for 1.5 h and

dried in the same vacuum at elevated temperature (60 °C) for 4 h. Thin films of MePcs up to 10nm were evaporated in Ultra High Vacuum (UHV) conditions (P ~ 1x 10^{-9} mbar) from an effusion cell kept at ~ 420°C.

The transistor structures consist of source-drain Au electrodes on a Si (n++)/SiO₂ substrate with an Al backgate. Using interdigitated electrode geometries with gate lengths L = 2, 5, 10 and 30µm and channel width W in the millimeter range, ratios W/L ~10³ were obtained. Representative results are shown in *figures II.3.2* and *II.3.3*.



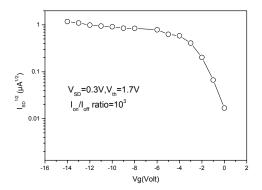


Fig. II.3.2: Characteristics of a sulfonated cobalt Pc p-type transistor prepared by spin coating. The gate oxide is 82nm and the gate length $L=10\mu m$. The mobility resulting from conventional analysis is 0.005 cm²/V.s

Fig. II.3.3: Square root of source-drain current vs gate voltage at the onset of saturation. The current on/off ratio is $\sim 10^3$ and the threshold voltage is 1.7Volts.

The knowledge of the barrier heights at interfaces between the electrodes and the active organic layers is of great importance for understanding and improvement of organic semiconducting devices. The electronic structure of the metal phthalocyanines/Au interface was investigated by X-ray and UV Photoelectron spectroscopies. The band energy diagram of the interface was obtained, from which the hole and electron injection barriers were determined.

c) Electronic transport in the atomic limit.

N. Papanikolaou

Manufacturing electronic devices using molecules and individual atoms is probably the ultimate limit of integration. Despite the fact that molecular electronic devices have been demonstrated over the last few years, many questions remain towards the realization of molecular electronic circuits. In the atomic limit, the usual laws of electronics like Ohms law are no longer valid. Instead, electronic transport is ballistic and coherent electron waves obey the laws of quantum mechanics. We study theoretically the electronic transport through single-atom contacts connected to two leads using ab-initio electronic structure calculations, without any adjustable parameters. The local density approximation to the density functional theory is used to map the many interacting electron problem to a single electron approximation. Ballistic transport is described within the Landauer approach. We are interested in the influence of the leads to the transport properties, as well as the effect of geometrical structure of the nanocontact and study electronic transport through different atoms.

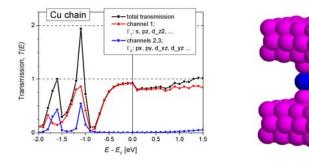


Fig. II.3.4: Calculated transmission coefficient though a Cu nanojunction. The atomic geometry of the constriction is shown on the right.

PUBLICATIONS in INTERNATIONAL JOURNALS

- "Tunneling and negative resistance effects for composite materials containing polyoxometalate molecules", G. Chaidogiannos, D. Velessiotis, P. Argitis, P. Koutsolelos, C. D. Diakoumakos, D. Tsamakis and N. Glezos, *Microel. Eng.* 73-74, 746 (2004)
- "Magnetoresistance of atomic-sized contacts: An ab initio study", A. Bagrets, N. Papanikolaou and I. Mertig, *Phys. Rev.* B 70 064410, (2004)
- "Korringa-Kohn-Rostoker Green-function formalism for ballistic transport", P. Mavropoulos, N. Papanikolaou and Ph. Dederichs, *Phys. Rev. B* 69 125104 (2004)
- "Spin-dependent transport in ferromagnet/semiconductor/ferromagnet junctions: a fully relativistic approach", V. Popescu, H. Eberrt, N. Papanikolaou, R. Zeller and Ph. Dederichs, *J. Phys: Condens. Mat.* 16 (48) p. S5579-S5586 (2004)

PUBLICATIONS in CONFERENCE PROCEEDINGS

- "Poly [(ethylenedioxy) thiophene] conductive films", M. Biler, L. T. D. Dvorakova, S. Nespurek and N. Glezos, World Polymer Conference, 40th Symposium on Macromolecules, Paris 2004
- 2. "Quantum effects in molecular nanodevices based on tungsten polyoxometalates", D. Velessiotis, G. Chaidogiannos, N. Glezos and P. Argitis, *European Microelectronics and Packaging Symposium, Prague* 2004

PARTICIPATION in CONFERENCES

 "Compound polymeric materials in molecular nanodevices: Electrical behavior of zero-dimension semiconducting inorganic molecules embedded in a polymer substrate", D Velessiotis, V Ioannou-Sougleridis, G Chaidogiannos and N. Glezos, MMN Conference, Athens 2004

DIPLOMA THESIS

"Electronic structure properties of Si nanosructures", P. Xidi, Completed in September 2004, presented at the University of Athens, Physics Department.

PROGRAM III

SILICON SENSORS and MICROSYSTEMS

Project III. 1: MICROMACHINED SILICON SENSORS and MICROSYSTEMS

Project leader: A. G. Nassiopoulou

Other key researchers: C. Tsamis, A. Tserepi, I. Raptis, P. Normand and H. Contopanagos Post-doctoral scientists: D. Goustouridis, S. Hatzandroulis Phd students: D. Pagonis, S. Polymenakos External collaborations: D. Tsoukalas (NTUA), G. Kaltsas (TEI of Athens)

Projects Running:

- EU, IST, IP : Goodfood, contract Nº: 508774
- "Remon Medical", Industrial cooperation
- Greek-Polish cooperation
- Archimedes (collaboration with TEI of Piraeus)
- Pythagoras (collaboration with the University of Patras)
- Joint project with the University of Cyprus "Photothermal detection of hydrogen"

Main objectives:

- Development of silicon micromachined processes
- Development of novel silicon sensors based on new materials and new processes
- Design, fabrication and testing of microsystems using silicon sensors.

Main results in 2004:

a) Porous silicon technology

Porous silicon is fabricated on a silicon wafer by electrochemical dissolution of bulk silicon. It may be formed locally on a silicon substrate as a thin or thick membrane, through a masking layer.

Due to the porous structure of the material, it provides thermal and electrical isolation and it may be used in different sensor applications.

a₁) Porous silicon-sealed microchannels in silicon

D. N. Pagonis, G. Kaltsas and A. G. Nassiopoulou

An electrochemical process has been developed for the fabrication of sealed air cavities and capped microchannels of different designs on a silicon wafer. The capping material is a porous silicon membrane which is planar to the silicon substrate. Two interesting applications of this technology are targeted: a) The effective local thermal isolation on a silicon wafer for use in micromachined thermal sensors, b) The potential use of this technology in the fabrication of microfluidic devices. An example of a microchannel in silicon sealed with porous silicon is shown in *fig. III.1.1*

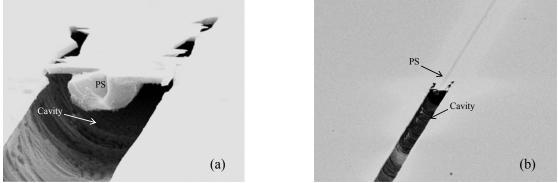
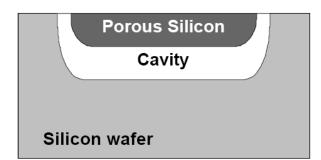


Fig. III.1.1: Top view SEM images of a microchannel in a silicon wafer, sealed with porous silicon. In both (a) and (b) the porous silicon sealing has been partially removed in order to uncover the channel's inner surface.

a₂) Porous silicon micro-hotplate technology

D. N. Pagonis, G. Kaltsas and A. G. Nassiopoulou

An improvement of porous silicon technology for local thermal isolation on bulk crystalline silicon has been achieved in 2004. The technique used consists of forming an air cavity below the porous layer to increase the thermal isolation efficiency (*fig. III.1.2*). Both porous silicon and the cavity underneath are formed during the same electrochemical process in two steps: in step 1 the current density used is below a critical value, and in step 2 it is switched to a value above the critical current for electropoliching. In this way, porous silicon is formed first, followed by the formation of the cavity underneath. An SEM image of such structure is shown in *fig. III.1.3*.



isotropic formation of the cavity. Due to the isotropic process, silicon etching occurs under the PS membrane and also under the surrounding mask, resulting in degredation of the membrane. To overcome this effect, a detailed study on the nature of the masking layer was performed to constrain silicon etching underneath the surrounding masking layer.

Fig. III.1.2: Schematic presentation of the

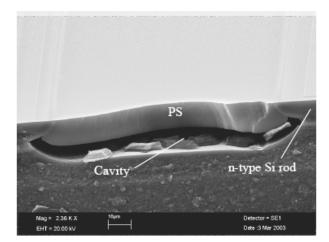


Fig. III.1.3: SEM image of a cross section of a porous silicon freestanding membrane with a cavity underneath.

b) Chemical Sensors

i. Metal Oxide Sensors

b.i.1. Optimization of micro-hotplates for low power chemical sensors-Characterization at reduced pressures

K. Spyropoulou^{*} and C. Tsamis

(^{*} MSc graduate student)

One major requirement for the fabrication of low power sensors, especially for integration in arrays, is the reduction of thermal losses. This can be achieved by the fabrication of the active elements of the sensors on suspended structures (micro-hotplates). Two different types of micro-hotplates have been used in the literature: The closed-type membrane, where the membrane overlaps the silicon substrate along its periphery and the suspended-type membrane, where the membrane is supported on the Si substrate by means of supporting beams. In the latter case, the thermal losses to the substrate take place only through the supporting beams, and thus they are minimized compared to the closed type membrane.

During this year, we performed a systematic study of various thermal isolation techniques. Combined experimental and simulation results using Coventorware (*Fig. III.1.4*) were used in order to estimate material properties such as thermal conductivity and to optimize micro-hotplate design. Measurements were performed at reduced pressures in order to minimize the parameters involved during modeling and to achieve better estimation of the thermal conductivity. For sufficiently low pressures, thermal losses in air can be minimized and thus ignored during the analysis of the *results* (*Fig. III.1.5*). As an example, two different isolation techniques, one using a thick porous silicon layer directly grown on the silicon substrate and the other using a thin suspended porous silicon micro-hotplate, were evaluated. A unique value of PS thermal

conductivity was estimated and it was found to fit the experimental results for the different sensor designs that were characterized.

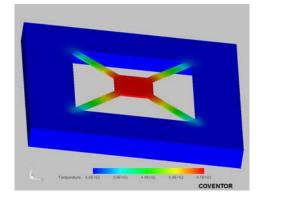


Fig. III.1.4: Temperature distribution of a suspended micro-hotplate, as predicted by Coventorware

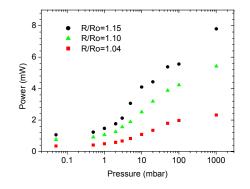


Fig. III.1.5: Power required to maintain the same change of the heater resistance (and thus the temperature) as a function of the ambient pressure.

b.i.2 The influence of thermal treatment on the stress characteristics of suspended Porous Silicon membranes on silicon

D. Papadimitriou*, C. Tsamis and A. G. Nassiopoulou

(* SEMFE/NTUA)

Over the last years, porous silicon (PS) has attracted significant interest, due to its potential usage in various fields of applications. PS layers have been effectively used for local thermal isolation on bulk silicon and as materials of suspended micro-hotplates for low power thermal sensors. Optimization of the mechanical properties of PS layers as well as stress control is a main issue that has to be considered for most of these applications.

During this year, we investigated in a systematic way the evolution of the stress that develops in PS layers as a function of porosity and thermal treatment for various micro-hotplate designs (*fig. III.1.6*). Micro-Raman spectroscopy was used for stress characterization in two cases: (a) for supported and (b) for suspended PS layers (*fig. III.1.7*). Stress-analysis based on these spectra reveals that membranes treated in an inert ambient, at moderate temperatures, are less strained and do not break when they are released from the substrate. The information obtained is useful for optimizing the fabrication process and the design of the devices.

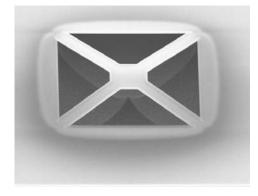


Fig. III.1.6: Fully released porous silicon micro-hotplate used as test structure for the stress measurement. The thickness of the membrane is $4 \mu m$.

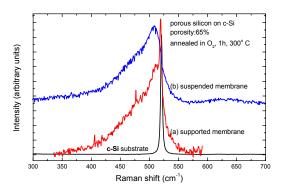


Fig. III.1.7: Raman spectra of (a) supported and (b) suspended PS membrane of porosity 65% after annealing at $300^{\circ}C$ for 1h in O_2 ambient. A spectrum of the c-Si substrate is also shown.

b.i.3. Control Circuit Design for MOX sensors

S. Chatzandroulis, D. Tassopoulos, P. Roubogiannakis and C. Tsamis

This activity includes the design of the control and reading electronics for metal oxide chemical sensors. MOX sensors consist of a heater resistance R_h and a chemically sensitive resistance R_s . The interface has to operate in a wide resistance range which could be between 300 Ohms and 20 Mohms, depending on the catalytic material used. Furthermore, it should be able to operate with sensor heaters made either of Pt or polysilicon. An electronic board, able to handle up to 4 sensors, has been implemented using discrete components. For the measurement of the sensitive resistance, Rs is placed in a voltage divider with selectable range resistors and is periodically sampled by the microcontroller ADC. Then the Rs value is calculated on the AVR and transmitted to the PC via the RS232. To drive the heater to the required temperature, a dedicated power circuit, which is controlled from the PWM output of the microcontroller, is used. To regulate the heater temperature, the heater resistance R_h is sampled periodically by the AVR which then decides to either increase or decrease the PWM output. *Fig. III.1.8* shows the above electronic circuit using discrete components.

Furthermore, an ASIC containing all of the analog electronics necessary to control and read 4 MOX sensors is under development.

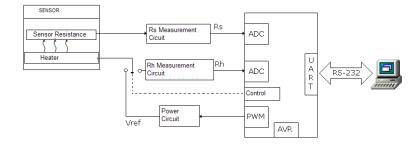


Fig. III.1.8: MOX Control and Reading Circuit using discrete components.

b.ii. Bimorph Chemical Sensors

b.ii.1. Design and Fabrication of Bimorph Chemical Sensors

S. Chatzandroulis, D. Goustouridis, J. Fraggakis*, S. Polymenakos, I. Raptis, D. Tsoukalas (SEMFE/NTUA) and P. Normand

(^{*} MSc graduate student)

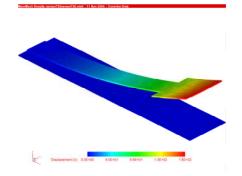
The activity aims at the development of a bimorph chemical sensor array for use in aroma recognition in e-nose applications. To this end, a new technology based on the bending of single-crystal silicon/polymer bilayers for the fabrication of selective chemical sensors, has been developed. The device utilizes a thin silicon microstructure, which could be a thin Si membrane or cantilever, covered by polymers like PMMA, PHEMA, PVAc, EPN etc, as chemical sensing layers. Of special interest, in this respect, were patternable polymer materials (e.g. PMMA, PHEMA), since the use of such materials facilitates the construction of bimorph chemical arrays. When the device is exposed to a volatile organic compound (VOC) concentration (e.g. methanol, ethanol) the overlying polymer swells forcing the silicon microstructure to bend and approach the substrate. This bending is then detected as a capacitance change in function with VOC ambient concentration.

Optimization of initial devices has followed two routes: one focusing on the geometric characteristics of bimorph sensors and one focusing on the understanding of polymer/analyte kinetics and swelling properties. For the first activity, extensive simulations of cantilever type devices have been performed using Coventorware® (*fig. 111.1.9*). Cantilevers of various lengths (ranging from 100 μ m to 2500 μ m) have been studied and a finite element (FE) model has been developed to facilitate the design and optimization of these devices. Experimental behavior is approximated by taking into account the stress induced in the cantilever due to the polymer swelling (*fig. 111.1.0*). Simulation results are in good agreement with experimental values.

Furthermore, within the second activity, a new method has been developed to engineer PHEMA swelling properties using controlled deep UV exposures. The new method allows for the modification of sensor sensitivity using this polymer.

b.ii.2. Polymer Materials for Chemical Sensors

D.Goustouridis, S.Chatzandroulis, K.Manoli*, M.Sanopoulou (IPC) and I.Raptis (* MSc graduate student)



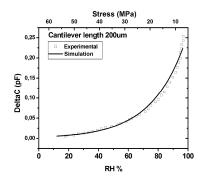
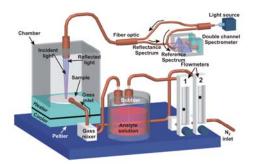


Fig. III.1.9: FE model: Displacement of the Si/polyimide bimorph cantilever.

Fig. III.1.10: Comparison between simulated and experimental data for a 200 µm long cantilever

Optimization of bimorph chemical sensors relies, in great part, on the understanding of the physicochemical properties of the chemically sensitive materials deposited onto the micromechanical silicon structure. To this end, a new white light interferometric experimental setup has been developed (*fig. III.1.11*). The setup is built around a chamber where controlled concentrations of volatile organic compounds may be introduced and allows the in-situ measurement of polymer layer thickness during analyte exposure with better than 0.5nm accuracy. The research focused on two well known polymer materials: PHEMA and PMMA. The two materials exhibit different, normalized to thickness, expansion to various volatile organic compounds, depending on the combination of the polarity and hydrogen bonding capability of the analyte. A wide polymer film thickness (50 and 600nm) range was examined and it was revealed that the normalized film expansion in both PHEMA and PMMA is nearly constant for films thicker than 100nm and increases for thinner films.



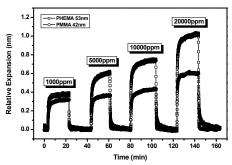


Fig. III.1.11: Polymeric film characterization apparatus.

Fig. III.1.12: Film thickness evolution vs. methanol vapor concentration for PHEMA, PMMA.

Also within this activity a new methodology to engineer the swelling properties of PHEMA using UV irradiation has been discovered *(fig. III.1.13)*. The new methodology allows for the modification of sensor sensitivity and aims at the construction of diversified chemical bimorph arrays using just one polymer.

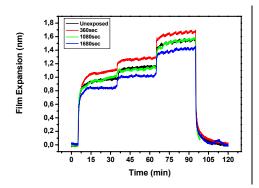


Fig. III.1.13: Swelling behavior of four PHEMA films (140nm) treated with different DUV exposure conditions as a function of methanol concentration (0, 5000, 10000 and 20000ppm)

c) Capacitive-type Micromechanical Silicon Sensors

D. Tsoukalas, S. Chatzadroulis, D. Goustouridis and P. Normand

During 2004 the industrial cooperation in the field of pressure sensors was carried on by completing the delivery of a first order of 10.000 units and the development of a new improved version of the device according to new specifications.

Also in 2004 the patent application to USPTO came to an agreeable end by the issue of U.S patent no 6,704,185. The procedure is also in progress in other countries.

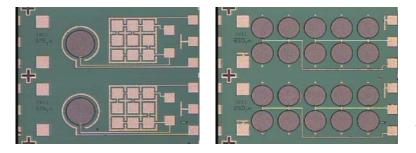


Fig. III.1.13: Capacitive type silicon sensors

d) Porous silicon CMOS-compatible on-chip resonators

H. Contopanagos and A. G. Nassiopoulou

A comprehensive approach for designing on-chip resonators using low-loss porous-silicon technology has been developed. We have focused on technology parameters that can be integrated within a standard CMOS process, such as a 0.13 micron CMOS and have targeted optimization of fundamental RF building blocks of direct interest to wireless communications chips.

First, we have designed optimized on-chip inductors with maximized quality factors, using electromagnetic simulations based on Method-of-Moment or Finite-Elements computer codes to obtain the optimum metallization for minimizing physical loss and maximizing the quality factors. In general, we predict a quality factor enhancement of about a factor of 2 when using porous Si, relative to standard CMOS of same metal thickness. These calculations were performed assuming certain electrical characteristics of porous Si as reported in the literature. The enhancement is due to both, shielding of the lossy Si substrate achieved by a thick porous silicon layer, and custom metal design of the inductor relative to standard designs found in the literature. In the future we will make these prototypes on porous silicon fabricated and electrically characterized at IMEL, and we will use those material parameters for the designs presented here.

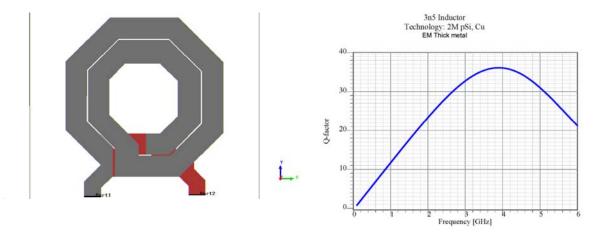


Fig.III.1.14: 2-metal-layer optimized inductor design on porous-Si for an inductance value L=3.5 nH and its predicted quality function in microwave frequencies for Bluetooth/WLAN systems.

Second, we have synthesized more complicated systems, and in particular pass-band filters integrated on-chip, using the previous high-Q inductors. Traditional passive LC filters can not be realized on standard CMOS technology because of the loss created by the Si substrate, in addition to the metal losses. Other difficulties with on-chip realizations, in addition to the losses, derive from the high-frequency coupling of each filter element to the substrate and from the parasitic electrical quantities developed in lay-out at the scale of CMOS technologies for RFICs. We dissect these physics and design issues and show how one can synthesize successfully on-chip filters on a low-loss porous-Si substrate which can be included in a standard process flow in CMOS. We quantify, feed back into the design and optimize all quantities produced by the material lay out and physical properties of this technology. This year's results appear promising in arriving at completely passive on-chip filters. If these are successfully realized, they will not suffer from the substantial noise problems that plague active integrated filter solutions currently available.

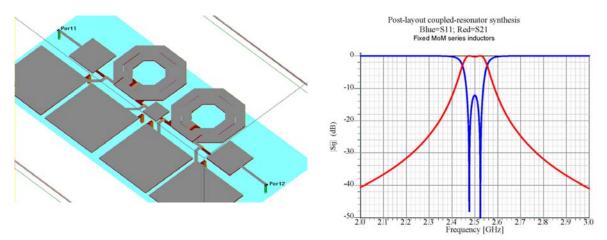


Fig.III.1.15: Simulated Bluetooth passive pass-band filter layout based on coupled resonator synthesis and post-layout response (with only reactive parasitics extracted).

Work in progress involves efficient simulation of the complete filter block with all losses present and fabrication and characterization of materials and prototypes based on above synthesis results.

Finally, 3 U.S. patents were issued in 2004 on inventions related to the above topics, see PATENTS.

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- "Capacitive Type Chemical Sensors Using Thin Silicon/Polymer Bimorph Membranes", S. Chatzandroulis, E. Tegou, D. Goustouridis, S. Polymenakos, D. Tsoukalas, Sensors and Actuators B: Chemical, Volume 103, Issues 1-2, 29 September 2004, Pages 392-396
- 2. "Fabrication of Chemical Sensors based on Si/polymer bimorphs", S. Chatzandroulis, E.Tegou, D. Goustouridis, S. Polymenakos, D. Tsoukalas, Microelectronic Engineering, Volumes 73-74, June 2004, Pages 847-851
- 3. "Polymeric film characterization for use in Bimorph Chemical Sensors", S.Chatzandroulis, D.Goustouridis, I.Raptis, accepted for publication in Microelectronic Engineering
- "Characterization of Polymer Layers for Silicon Micromachined Bilayer Chemical Sensors Using White Light Interferometry", D. Goustouridis, K. Manoli, S. Chatzandroulis, M. Sanopoulou, I. Raptis accepted for publication in Sensors and Actuators B
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- 9. "Gas flow meter for applications in medical equipment for respiratory control-Study of the package and housing" G. Kaltsas and A. G. Nassiopoulou, Sensors & Acruators A, 100, 413-422 (2004)

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- "A microcontroller-based interface circuit for data acquisition and control of a micromechanical thermal flowsensor", P. Asimakopoulos, G. Kaltsas and A. G. Nasisopoulou, International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece, *To appear in Journal of Physics: Conference Series*
- 3. "Simultaneous use of flow and pressure sensors for flow determination in both laminar and turbulent regions", G. Kaltsas, D. Goustouridis, A. G. Nassiopoulou and D. Tsoukalas, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece

- 4. "Investigation of different operation modes of a micromechanical thermal flow sensor, using a microcontrollerbased interface circuit", P. Asimakopoulos, G. Kaltsas and A. G. Nassiopoulou, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- "Stress characteristics of suspended Porous Silicon microstructures on silicon", K. Anestou, D. Papadimitriou, C. Tsamis and A.G. Nassiopoulou, *International Conference on Microelectronics, Microsystems and Nanotechnology* (MMN 2004), November 14-17, Athens, Greece
- 6. "A CMOS compatible thermal accelerometer without solid proof mass, based on porous silicon thermal isolation", G. Kaltsas, D. Goustouridis and A. G. Nassiopoulou, *IEEE Sensors 2004*, Vienna, Austria, October 24-27, 2004
- "A CMOS compatible process for porous silicon/air cavity formation for application in thermal sensors and microfluidic devices", D. N. Pagonis, A. G. Nassiopoulou and G. Kaltsas, 4th Int. Con. 4th Int. Con. On Porous Semiconductors Science and Technology (PSST 2004), Cullera-Valencia, Spain, March 14-19, 2004
- "Porous silicon micro-hotplates for low power thermal sensors. Measurements at reduced pressures and estimation of porous silicon thermal conductivity of porous silicon", C. Tsamis, K. Spyropoulos and A.G. Nassiopoulou, 4th Int. Con. On Porous Semiconductors Science and Technology (PSST 2004), Cullera-Valencia, Spain, March 14-19, 2004
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- "Modification Of Polymer Swelling By UV Irradiation For Use In Chemical Sensing", D. Goustouridis, S. Chatzandroulis, I. Raptis, E.S. Valamontes, *IEEE SENSORS 3rd Int. Conference on Sensors, Vienna, Austria, Oct.* 24-27, 2004
- 13. "Simulation of Capacitive type Bimorph Humidity Sensors", J. Fragakis, S. Chatzandroulis, D. Papadimitriou, C. Tsamis, "MMN 2004, 15-17 November 2004 Athens, Greece
- 14. "Polymeric film characterization for use in bimorph chemical sensors", S. Chatzandroulis, D. Goustouridis, I. Raptis, MMN 2004, 15-17 November 2004 Athens, Greece
- 15. "Porous silicon micro-hotplates for low power thermal sensors. Measurements at reduced pressures and estimation of porous silicon thermal conductivity", C. Tsamis, K. Spyropoulou and A. G. Nassiopoulou, 4th International Conference on "Porous Silicon Science and Technology", PSST 2004, March 2004, Valencia, Spain (Oral presentation)
- "Stress characteristics of suspended Porous Silicon microstructures on silicon"K. Anestou, D. Papadimitriou, C. Tsamis and A. G. Nassiopoulou, 2nd Conference on Microelectronics, Microsystems, Nanotechnology, MMN 2004, 15-17 November 2004, Athens, Greece (Poster presentation)
- 17. "Wheeler's law and related issues in Integrated Antennas", H. Contopanagos, S. Rowson and L. Desclos, published in 2004 *IEEE Antennas and Propagation Society International Symposium Digest*, (June 20-26, 2004, Monterey, CA).
- "Electromagnetic design methods in systems-on-chip: Integrated filters for wireless CMOS RFICs" H. Contopanagos, to appear in *Journal of Physics: Conference Series, International Conference on Microelectronics, Microsystems and Nanotechnology* (MMN 2004, November 14-17, Athens, Greece).

INVITED TALKS

- "Porous silicon for sensor applications", A. G. Nassiopoulou, Invited talk, NATO Advanced Study Institute on Nanostructured and Advanced Materials for Optoelectronic, Photovoltaic & Sensor applications, Sozopol, Bulgaria, September 6-17, 2004
- "Electromagnetic design methods in systems-on-chip: Integrated filters for wireless CMOS RFICs" H. Contopanagos, Invited talk, International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004, November 14-17, Athens, Greece).

Msc THESES

K. Spyropoulou, "Modeling and optimization of micro-hotplates for thermal sensor applications" (Msc Course in Microelectronics, Univ. of Athens, Responsible: C. Tsamis)

PATENTS

- 1. U.S patent Nº 6,704,185, Mar. 9, 2004, "Capacitive Pressure Responsive Devices and Their Fabrication"
- 2. US Patent Nº 6,812,544 November 2, 2004, "Integrated circuit having oversized components", H. Contopanagos and C. Komninakis
- US Patent Nº 6,809,623 October 26, 2004, "High Q on-chip inductor", S. Kyriazidou, H. Contopanagos and R. Rofougaran
- US Patent N^o 6,709,977 March 23, 2004, "Integrated circuit having oversized components and method of manufacture there of ", H. Contopanagos and C. Komninakis

PROGRAM III

SILICON SENSORS and MICROSYSTEMS

Project III. 2: BIO-MICROSYSTEMS

Project leader: K. Misiakos

Other key researchers (from the Institute): P. Argitis, E. Gogolides, A. Tserepi, G. Raptis and H. Contopanagos

PhD candidates: M. Vlachopoulou

Projects Running:

- IST-2000-28214, BIOMIC

<u>Goals</u>

- Integrated Optical Bioanalytical Devices

Main results (2004): SNP detection in DNA arrays, cardiac marker detection and label-free protein detection

The monolithic optoelectronic bio-transducer developed at IMEL was optimized and coupled to a fluidic module (see *fig. III.1.1*).

Fig. III.2.1 shows a schematic of the transducer and the aligned fluidic cover. A packaged device is shown in fig. III.2.3, while figs. III.2.4, and III.2.5 show characterization results.

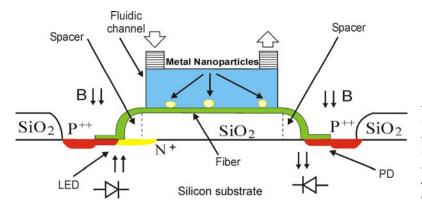


Fig. III.2.1: Schematic illustration showing the monolithic optoelectronic biotransducer coupled to a fluidic module. This fluidic module is shown below and covers in series all nine fibers per chip.

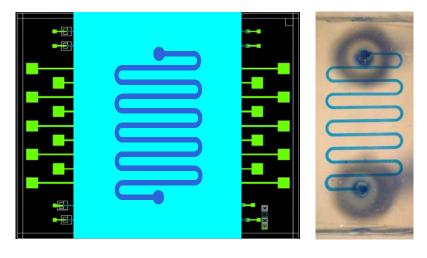
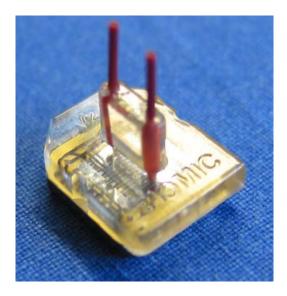
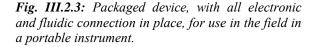


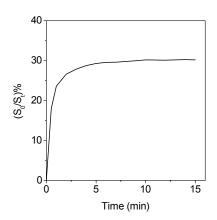
Fig. III.2.2: Schematic (top view) of the transducer and the aligned fluidic cover (left). On the right, a photo the fluidic cover is shown with a blue dye liquid inside the channel.





The analytical capabilities of the device were demonstrated by performing a non-competitive immunoassay for the MB isoform of the creatinine kinase enzyme (CK-MB). CK-MB is one of the most widely used markers for the early diagnosis of cardiac infarction. Also it was demonstrated by the detection of DNA single nucleotide polymorphism

25



20 Signal Drop 15 10 % 5 0 8 2 3 5 6 9 10 4 7 Fiber No

Fig.III.2.4: Real-time response plotted as the ratio of the initial detector photocurrent (S_0) to the instantaneous photocurrent (S_t) . The CK-MB concentration 300 ng/mL.

Fig. III.2.5: Signal obtained from the 9 fibers of a single chip after hybridization. Odd fibers were modified with full-matching sequences and even fibers with single base mismatching sequences

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- 1. "Protein patterning by micromachined silicon embossing on polymer surfaces", Goustouridis D, Misiakos K, Petrou P S, Kakabakos S E, *Applied Physics Letters 85* (26): 6418-6420 (2004)
- "Selective plasma-induced deposition of fluorocarbon films on metal surfaces for actuation in microfluidics", Bayiati P, Tserepi A, Gogolides E, Misiakos K, *Journal of Vacuum Science & Technology A* 22 (4): 1546-1551 (2004)
- 3. "A monolithic silicon optoelectronic transducer as a real-time affinity biosensor", Misiakos K, Kakabakos S E, Petrou P S, Ruf H H, *Analytical Chemistry* 76 (5): 1366-1373 (2004)

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- "Laser ablation of polymeric layers for fabrication of biomolecule microarrays" P. S. Petrou, A. Douvas, S. E. Kakabakos, K. Misiakos, P. Argitis, E. Sarantopoulou, Z. Kollia and C. Cefalas, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 33
- "Sub-10 μm protein microarrays fabricated using new near UV photoresist and novel multi-step lithographic scheme", M. Chatzichristidi, A. Douvas, K. Misiakos, I. Raptis, C. D. Diakoumakos, P. Petrou, S. E. Kakabakos and P. Argitis, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 32

- "Printing protein patterns". K. Misiakos, D. Goustouridis, S. Kakabakos, P. Petrou. 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 38
- "Multianalyte integrated optical biosensors based on monolithic silicon optoelectronic transducers" K. Misiakos, S. Kakabakos, P. Petrou and H. Ruf, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 60
- "Development of a capillary-based fluoroimmunosensor capable for real-time measurement of the analytical signal", C. Mastichiadis, S. E. Kakabakos, P. S. Petrou, I. Christofidis and K. Misiakos, 2nd International Workshop on Multianalyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 70
- "Fabrication of microscale protein arrays for low crosstalk electrochemical sensing", A. Bush, I. Katakis, M. Chatzichristidi, K. Misiakos and P. Argitis, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 36
- "Plasma-deposited fluorocarbon films for use in actuation of fluid movement in microfluidic devices", Bayiati P., Tserepi A, Gogolides E, Misiakos K, Abstract p. 67

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- "A bioanalytical microsystem for protein and DNA sensing based on a monolithic silicon optoelectronic transducer", K. Misiakos, P.S. Petrou, S.E. Kakabakos, H. H. Ruf, T. Knoll, E. Ehrentreich-Foerster and F.F. Bier, *Second Conference on Microelectronics Microsystems and Nanotechnology*, Athens, Greece, 15-17 November, 2004
- "New lithographic process and resist capable for fabrication of submicron protein microarrays", Chatzichristidi M., Douvas A., Misiakos K., Raptis I., Diakoumakos C. D., Argitis P., Petrou P. S. and. Kakabakos S.E, Second Conference on Microelectronics Microsystems and Nanotechnology, Athens, Greece, 15-17 November, 2004

PATENT APPLICATIONS IN 2004

- 1. "Integrated optoelectronic silicon biosensor for the detection of biomolecules labeled with chromophore groups or nanoparticles", K. Misiakos and S. Kakabakos, European patent EP 1448978
- 2. "Photoresists processable under biocompatible conditions for multi-biomolecule patterning", P. Argitis, K. Misiakos, S. Kakabakos, A, Douvas and C. Diakoumakos, **European patent EP 1395878**

CONFERENCE ORGANIZATION

2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004

PROGRAM III

SILICON SENSORS and MICROSYSTEMS

Project III. 3: THIN FILM DEVICES for LARGE AREA ELECTRONICS

Project leader: D. N. Kouvatsos

PhD candidates: M. Exarchos, L. Michalas (University of Athens)

Projects Running:

- Research grant from Sharp Laboratories of America. 2003-2005
- Greece-Serbia 2004-2006 bilateral research project.

<u>Goals:</u>

This research aims at the optimization of the active layer of polysilicon films obtained using advanced excimer laser crystallization methods and of the resulting performance parameters of thin film transistors fabricated in such films. Specifically, the targets are:

- Evaluation of device parameter (a) hot carrier and (b) irradiation stress-induced degradation and identification of ageing mechanisms in TFTs fabricated in advanced excimer laser annealed (ELA) polysilicon films. Investigation of polysilicon active layer defects using transient drain current analysis in ELA TFTs.
- Investigation of the influence of film thickness and crystallization technique on defects and on device degradation for ELA technology optimization.
- Evaluation of bias stress-induced instabilities in solid phase crystallized (SPC) TFTs.

Main results:

The results obtained to date can be summarized as follows:

a) Hot carrier stress degradation

Superior hot carrier stress endurance has been demonstrated for ultra-thin film ELA TFTs as compared

to ones in typical 50 - 100 nm films. Two ageing mechanisms have been identified (corresponding to ΔV_{th} power law exponents of ~0.2 and ~0.5, respectively): hot-carrier injection in the gate insulator and deep-state generation in the active device "body". The relative dominance of degradation mechanisms has been ascribed to charged defect field and partial depletion effects. The trap densities Nt and Dts, extracted from a Levinson analysis and from the subthreshold swing s, respectively, are insensitive to stress for TFTs in ultra-thin SLS ELA polysilicon films. A vertical channel orientation relative to the direction of the elongated grains results in a suppressed interfacial (expressed in s and g_m) degradation rate, as compared to a parallel one. Fig. III.3.1 shows: degradation Δs vs. stressing time for TFTs parallel oriented in 30, 50 or 100 nm films, or vertically oriented in 100 nm films.

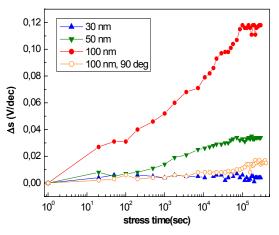


Fig. III.3.1: Degradation Δs vs. stressing time for TFTs parallel oriented in 30, 50 or 100 nm films, or vertically oriented in 100 nm films.

b) Transient drain current analysis

The observed, after the application of a gate bias pulse, drain current transients in SLS (sequential lateral solidification) ELA TFTs are of the same order of magnitude at dark as well as under illumination. Moreover, the DLTS signals $\Delta I_{DS}/I_{DS}$ fall sharply at low temperatures, indicating a carrier generation freezeout. From these characteristics, a low density of generation-recombination centers and a corresponding high crystalline quality of ELA polysilicon films crystallized by the SLS technique are inferred.

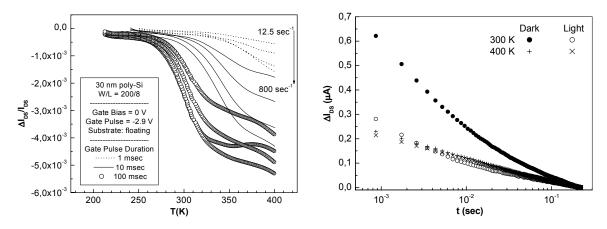


Fig. III.3.3: (Right) Drain current transients $\Delta I_{DS}(t)$ against time after end of the gate pulse. (Left) Normalized ΔI_{DS} against temperature (DLTS spectra), exhibiting freezeout.

From the observed shift, for various pulse durations, of the generation freezeout point a thermally activated generation process via a hole trap at 0.49 eV above E_V is inferred. Dislocation and RTA-related traps have been identified for TFTs fabricated with various SLS ELA techniques.

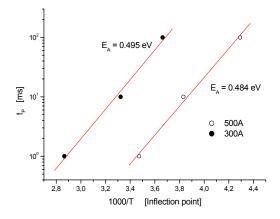


Fig. III.3.4: Arrhenius plot for the freezeout inflection point.

c) γ-irradiation induced degradation

TFTs in ultra-thin SLS ELA polysilicon films were found to exhibit significantly less pronounced γ -irradiation-induced degradation, as compared to TFTs in thicker films: less oxide/interface charge trapping (ΔN_{ot} and ΔN_{it}) and smaller subthreshold slope *s* degradation. Furthermore, significantly better threshold voltage stability was exhibited by TFTs in ultra-thin polysilicon films, while the mobility degradation was similar. The γ -irradiation-induced degradation was enhanced in the presence of a gate field.

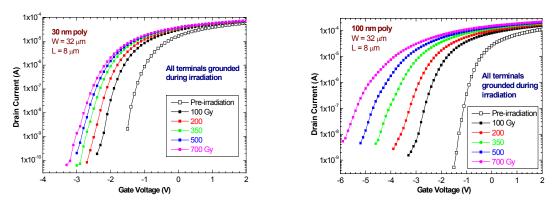


Fig. III.3.5: Transfer characteristics for y-irradiated 30 nm (left) or 100 nm (right) TFTs.

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- "Effects of hot carrier and irradiation stresses on advanced excimer laser annealed polycrystalline silicon thin film transistors", Kouvatsos, D. N., Davidovic V., Papaioannou G. J., Stojadinovic N., Michalas L., Exarchos M., Voutsas A. T. and Goustouridis D., *Microelectronics Reliability* 44 (9-11), 1631, (September 2004)
- 2. "Effect of silicon thickness on the degradation mechanisms of sequential-laterally-solidified polycrystalline silicon thin film transistors during hot-carrier stress", Voutsas, A. T., Kouvatsos D. N., Michalas L. and Papaioannou G. J., accepted to appear in *IEEE Electron Device Letters*
- 3. "The effect of Generation-Recombination mechanisms on the transient behavior of polycrystalline silicon transistors", Papaioannou, G.J., Voutsas A., Exarchos M. and Kouvatsos D., accepted to appear in *Thin Solid Films*

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- "Effects of DC gate and drain bias stresses on the degradation of excimer laser crystallized polysilicon thin film transistors", Kouvatsos, D. N., Michalas L., Voutsas A. T. and Papaioannou G. J., 2nd Conference on Microelectronics, Microsystems and Nanotechnology, Athens, Greece, (November 2004)
- "Investigation of drain current transient behavior in SLS TFTs with the DLTS technique", Exarchos M. A., Papaioannou G. J., Kouvatsos D. N. and Voutsas A. T., 2nd Conference on Microelectronics, Microsystems and Nanotechnology, Athens, Greece, (November 2004)

MSc THESES

- 1. "Investigation of hot carrier effects in polycrystalline silicon TFTs", L. Michalas, Physics Department, University of Athens
- 2. "Fabrication of MOS devices utilizing W or W/Cu metallization and characterization of MOS capacitors and TFTs", T. Nikas, Informatics Department, University of Athens

PROGRAM III SILICON SENSORS and MICROSYSTEMS

Project III. 4: CIRCUITS and DEVICES for OPTOELECTRONIC INTERCONNECTIONS

Project leader: G. Halkias

Other key researchers: S. G. Katsafouros PhD candidates: K. Minoglou M. Sc. student: V. Grivas External collaborators: E. Kyriakis-Bitzaros

Projects Running:

- E.U. IST PICMOS
- ESA, "Multigigabit Optical Backplane Interconnections"
- GSRT, MILI-A

Goals- Basic results:

The general goal of the project is the development of the necessary technologies for the future highdensity and high-speed optoelectronic interconnections. A recent parallel goal of the project is the successful implementation of optoelectronic technologies in spacecraft environment.

a) Development of a model for the simulation of Vertical Cavity Surface Emitting Lasers (VCSELs) and circuit topologies for the efficient driving of the device

A compact non-linear circuit model for the input of packaged high-speed VCSELs is presented. The model includes the thermal effects as well as the parasitics, due to the various levels of the packaging hierarchy, to ensure a realistic representation of the input of the VCSELs. The values of the model parameters are extracted from dc current-light-voltage characteristics and S_{11} vector measurements using a two-step parameter extraction procedure. Extraction of the model parameters and comparison between measured and simulated results have been performed for two different commercially available VCSELs operating at 2.5Gb/s. The achieved agreement between the measured and simulated results is very satisfactory for the dc as well for the S_{11} curves in the frequency range from 3MHz to 3GHz.

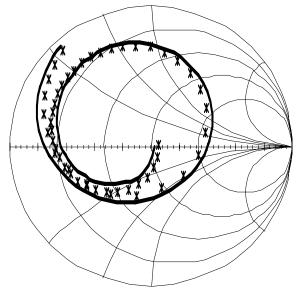


Fig. III.4.1: Measured and simulated VCSEL S₁₁ parameter

b) Multigigabit optical backplane for space applications

In this activity an optical backplane, able to function at multigigabit speeds, is studied and will be fabricated using space worthy Wavelength Division Multiplexing technologies. The project is executed in collaboration with IMEC (Belgium) and Intune Technologies Ltd (Ireland). The objectives of the program are demonstrated by a system depicted schematically in *fig. 111.4.2.* It consists of 4 nodes connected by an optical backplane. Two nodes have transmitting and receiving capability, while the other two can only receive so as to limit the number of lasers needed for the demonstrator. The system basically consists of three parts: the wavelength router, the transponders and the nodes generating or receiving data and implementing the control plane. Additionally, deciding which connections to set up, switching and monitoring of the backplane are controlled by a PC. Our main involvement in this project is the design and implementation, in a high-speed FPGA, of the backplane control unit as well as the real-time pseudo-random data generation and Bit-Error-Rate (BER) measurement capability for system evaluation and testing.

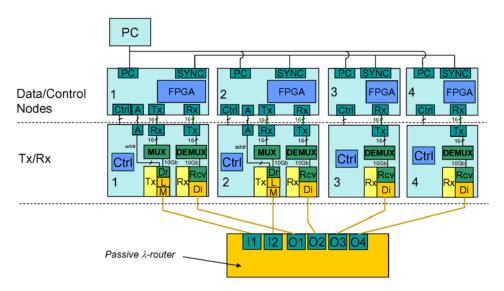


Fig. III.4.2: Block diagram of the multigigabit optical backplane

c) Heterogeneous integration of optical interconnections onto CMOS ICs

In this activity various methods for the heterogeneous integration of active optoelectronic devices (microlasers, photodiodes in III-V semiconductors) along with passive (waveguides) components onto deep submicron CMOS ICs are examined. Specifically, our goal is the development of a metallic bonding methodology using the appropriate alloy for the simultaneous mechanical attachment and electrical interconnection of the III-V photonic dies on the silicon circuits. The use of rare earth elements in the bonding alloy is investigated for the enhancement of the bonding strength and encouraging results have been obtained. The project is executed in collaboration with IMEC (Belgium), ST, CEA, CNRS-FMNT (France) and TUE (Holland) in the framework of the European project PICMOS.

PUBLICATIONS in INTERNATIONAL JOURNALS

- "Low temperature wafer bonding for thin silicon film transfer", D. Goustouridis, K. Minoglou, S. Kolliopoulou, S. Chatzandroulis, P. Morfouli, P.Normand and D. Tsoukalas, *Sensors and Actuators A: Physical* Volume 110, Issues 1-3, 401-406, (February 2004)
- "A compact non-linear equivalent circuit model and parameter extraction method for packaged high-speed VCSELs", K. Minoglou, E. D. Kyriakis-Bitzaros, D. Syvridis, G. Halkias, *IEEE Journal of Lightwave Technology*, Vol.22, No.12, pp.2823-2827, (December 2004)

PUBLICATIONS in CONFERENCE PROCEEDINGS

- 1. "Effects of Packaging Parasitics on High Speed operation of VCSELs", K. Minoglou, E. D. Kyriakis-Bitzaros, A. Arapoyanni and G. Halkias, *NEWCAS 2004*, pp.53-56 20-23 June 2004, Montreal, Canada
- "Development of a new parameter extraction methodology for the modeling of the input of the VCSELs", K.Minoglou, E. D. Kyriakis-Bitzaros, D. Syvridis, G. Halkias, *HETECH 2004, 13th European Workshop on Heterostructure Technology*, October 3-6, 2004, Heraklion, Crete, Greece

PARTICIPATION in CONFERENCES

"Metallic bonding of optoelectronic dies to silicon wafers", K. Minoglou, E. D. Kyriakis-Bitzaros, E. Grivas, S. Katsafouros, A. Kostopoulos, G. Konstadinidis and G. Halkias, "MMN 2004", November 14-17, 2004, Athens, Greece

EDUCATIONAL OUTPUT in 2004

a) PhD THESES

3 PhD theses completed in 2004. The following PhD theses carried out at IMEL the year 2004, were defended in Greek Universities:

- Vassilios Bellas
 Title: "Development of novel siloxane and polymeric materials for high resolution lithography. Structure-properties relationships"
 Department of Chemistry, University of Athens
 Supervisor: Dr. P. Argitis
 Defended at: February 2004
- Margarita Chatzichristidi
 Title: "Chemically amplified photoresist materials for the fabrication of Microsystems"
 Department of Chemistry, University of Athens
 Supervisor: Dr. P. Argitis
 Defended at: December 2004
- Dimitris-Nikolaos Pagonis
 Title: "Local silicon thermal isolation technology-application on a silicon flow sensor"
 Department of Informatics, University of Athens
 Supervisor: Dr. A. G. Nassiopoulou
 Defended at: February 2004

b) DIPLOMA THESES

- Diploma thesis: M.Sc., University of Athens. Name: Loukas Michalas Title: Investigation of hot carrier effects in polycrystalline silicon TFTs Defended at: Physics Department, University of Athens, 27-1-2005 Supervisor: D. Kouvatsos
- 2. Diploma thesis: M.Sc., University of Athens Name: Tasos Nikas Title: Fabrication of MOS devices utilizing W or W/Cu metallization and characterization of MOS capacitors and TFTs Defended at: IMEL, 10-11-2004 Supervisor: D. Kouvatsos
- Master of Science Thesis
 Name: Evangelos Th. Grivas
 Title: High Data Rate Optical Interconnections for Satellite Processing Systems.
 Defended at: Athens University, November 2004
 Supervisors: S.G. Katsafouros, G. Halkias
- 4. Diploma thesis (AEI): Bachelor's degree Name: Dimitris Kontziabassis Title: Fabrication of micromechanical structures with epoxy resists Defended at: University of Ioannina, Sept. 2004 Supervisor: E. Gogolides
- 5. Diploma thesis (AEI): Bachelor's degree Name: Vassilis Sarris Title: Simulation of the dissolution of thin polymer films for microlithography with stochastic models Defended at: National Technical University of Athens, November 2004 Supervisor: E. Gogolides

6. Diploma thesis (AEI) Name: I. Xidi Title: Electronic properties of Si nanostructures Defended at: Physics Department, University of Athens, date : September 2004 Supervisor: N. Papanikolaou

7. Diploma thesis (AEI): Bachelor's degree Name: Maria Kitsara

Title: Layer-by-layer UV micromachining methodology of epoxy based resist embedded microchannels Defended at: University of Ioannina, September 2004 Supervisor I. Raptis

c) LABORATORY TRAINING

- -
- Katsaros I., TEI of Athens Georga Th., TEI of Athens Makris K TEI of Athens
- -
- -Michailidis E., TEI of Athens
- Pappas D., TEI of Athens

INTERNATIONAL CONFERENCES ORGANIZED BY IMEL IN THE YEAR 2004

Three important International events were organized by IMEL in the year 2004

1. 13th NID MEL-ARI Workshop

The 13th NID Workshop on Nanoelectronic Devices was held at NCSR "Demokritos", Athens, Greece in February 4-6, 2004. The aim was to gather together participants of the projects funded by the European Union within the NID pro-active initiative. Presentations from the EU projects and invited talks from experts outside the NID initiative took place during the Workshop focussing on the application of a broad range of nanoscale technologies to information processing and on the perspectives for replacing mainstream approaches, such as CMOS, with novel approaches, after reaching the expected physical limits for miniaturization.

The Workshop was attended by 140 participants from different European and non-European countries. A one-day joint "Greek/PHANTOMS" Symposium on Nanotechnology was also held during the workshop, aiming at providing a research overview on activities carried out in Greece in this field.









Photos from the 13th NID Workshop

2. MMN 2004-International Conference on Microelectronics, Microsystems and Nanotechnologyheld at NCSR "Demokritos" on 14-17 November 2004

The second Conference on Microelectronics, Microsystems and Nanotechnology took place at the National Centre for Scientific Research "Demokritos", in Athens, Greece, between 14 and 17 November 2004. The Conference has been organized by the Institute of Microelectronics (IMEL) with the aim to bring together scientists and engineers working in the above exciting fields in order to interact and exchange ideas. During the three days of the conference there were 45 oral presentations including 9 invited papers. In total almost 130 papers were presented and the conference was attended by 146 participants from 16 countries. The topics covered were nanotechnologies, quantum devices, sensors, micro- and nano-systems, semiconductor devices, C-MOS fabrication and characterization methods, new materials for electronics, as well as IC design. A lot of interesting results were presented. Especially studies of metal and semiconductor quantum dots, both theoretical and experimental were presented, with emphasis on their applications in optoelectronics but also in nanocrystal memory devices that promise better scaling properties and sustain higher integration. Another interesting topic was new developments in biocompatible lithographic processes for applications in biosensors. In particular the need for new processes for lithography which can be used together with biological materials has been emhasized. Moreover innovations in Si sensors for biological applications in medicine and food industry were highlighted by one of the invited speakers, while another invited speaker gave an overview of recent developments and perspectives in ultimate CMOS technology. The conference covered also issues and concepts of IC design with two invited talks on RF design and cryptography. Finally, studies of new materials for nanotechnology applications like carbon nanotubes and magnetic nanoparticles, were also presented.

The conference included presentations from several companies active in this field in Greece in an effort to bring together academia with industry. The proceedings will be published after reviewing in a special issue of Journal of Physics: Conference Series.



Photos from MMN Conference, held at NCSR "Demokritos" in November 2004



Photos from MMN 2004 Conference



Photos from the the award ceremony to honor M. Hatzakisduring MMN 2004

3. *PSST-2004-4th International Conference on Porous Semiconductors Science and Technology-Held in Valencia on 14-19 March 2004.*

This conference was co-organized by A. G. Nassiopoulou (IMEL), L. Canham (Psi Medica) and V. Parkhutik (Technical University of Valencia)

It was the fourth of a series of conferences focussing entirely on porous semiconductors, including methods of fabrication, processing, properties and applications.

The conference was preceeded by a half-day of short cources on general issues of porous semiconductors, which intended to introduce newcomers into the various topics of the Conference.

The scientific programme included oral and poster presentations in 14 technical sessions.

The conference was intended by 220 participants from 42 countries. 170 papers were submitted for the Proceedings, to be published in Physica Status Solidi after peer review.



Photo of participants of PSST 2004

<u>ANNEX I: PERSONNEL</u>

Researchers

- 1. Nassiopoulou A., Director
- 2. Argitis P.
- 3. Davazoglou D.
- Glezos N. 4.
- 5. Goggolides E.
- Halkias G. 6.
- 7. Katsafouros S.
- Kouvatos D. 8.
- 9. Misiakos K.
- 10. Normand P.
- Papanikolaou N. 11.
- Raptis I. 12.
- 13. Tsamis C.
- 14. Tserepi A.
- 15. Tsoi E.

Research Assiciate

1. Contopanagos H.

Post Doctoral Scientists

from	Regul	lar Public	Budget

- Chatzandroulis S 1.
- 2. Douvas A
- Goustouridis D. 3.
- 4. Patsis G.
- 5. Skarlatos D.
- Vambakas V. 6.
- on Contract
 - Ioannou-Sougleridis V. 1.
 - 2. Konstandoudis K.
 - 3. Vassilopoulou M.

PhD Students

from Regular Public Budget

- Bayatti P. 1.
- 2. Chaidogiannos G.
- 3.

PhD Students

- Κοκονού Μ. 6.
- Minoglou K. 7.
- 8. Olzierski A.
- 9. Niakoula D
- Papadimitropoulos G. 10.
- Polymenakos S. 11.
- 12. Vlachopoulou M
- Vourdas N. 13.

on Contract

- Dimitrakis P. 1.
- 2. Grivas E.
- Kokoris G. 3.
- 4. Koliopoulou S.
- 5. Kotsovos K.
- Salonidou A. 6.
- Velessiotis D. 7.
- 8. Zoi A.

Technical and Administrative Personnel

from Regular Public Budget

- Lagouvardou M. 1.
- 2. Makridi Z.
- 3. Makridis Z.
- 4. Mavropoulis I.
- 5. Tsoromokos D.
- on Contract
- Bolomiti E. 1.
- 2. Boukouras K.
- 3. Georgiou C.
- 4. Linarakis E.
- Papakonstantinou C. P. 5.
- Sergis E. 6.
- Tokpasidou E. 7.



- Catzichristidi M.
- 4. Chronaios A.
- 5. Kelaidis N.

ANNEX II: PUBLICATIONS OF IMEL

A. PUBLICATIONS in INTERNATIONAL JOURNALS & REVIEWS

- "Polyhedral oligomeric silsesquioxane (POSS) acrylate copolymers for microfabrication: properties and formulation of resist materials", E. Tegou, V. Bellas, E. Gogolides and P. Argitis, Microelectronic Engineering, 73/74, 238-243, (2004)
- "Polyhedral oligomeric silsesquioxane (POSS) based resists: material design challenges and evaluation at 157 nm", E. Tegou, V. Bellas, E. Gogolides, P. Argitis, D. Eon, G. Catry, C. Cardinaud, *Chem. Mater*, 16, 2567-77, (2004)
- "Glass transition temperature monitoring in bilayer and patterned photoresist films", D. Niakoula, I. Raptis, D. Goustouridis, P. Argitis, Jpn. J. Appl. Phys., 43 (8A), 5247-8, (2004)
- "Surface segregation of photoresist copolymers containing polyhedral oligomeric silsesquioxanes studied by X-ray photoelectron spectroscopy", D. Eon, G. Cartry, V. Fernandez, C. Cardinaux, E. Tegou, V. Bellas, P. Argitis, E. Gogolides, J. Vac. Sci. Technol. B, 22, 2526-32, (2004)
- 5. "Evaluation of poly (hydroxyethyl methacrylate) imaging chemistries for micropatterning applications", M. Vasilopoulou, S. Boyatzis, I. Raptis, D. Dimotikalli, P. Argitis, *J. Mater. Chem.*, 14, 3312-20, (2004)
- "Development and molecular-weight issues on the lithographic performance of poly (methyl methacrylate)", A. Olzierski, I. Raptis, *Microelectron. Eng.* 73-74 244-251 (2004)
- 7. "Resists for nanolithography", P. Argitis, Encyclopedia of Nanoscience and Nanotechnology, H. S. Nalwa ed., American Scientific Publishers, (March 2004)
- "Line Edge Roughness (LER) investigation on chemically amplified resist (CAR) materials with masked helium ion beam lithography", S. Eder-Kapl, H. Loeschner, M. Zeininger, O. Kirch, G. P. Patsis, V. Constantoudis, and E. Gogolides, *Microelectronic Engineering*, 73-74, 252 (2004)
- 9. "Photoresist line-edge roughness analysis using scaling concepts", V. Constantoudis, G. P. Patsis, and E. Gogolides, J. Microlithogr. Microfabrication, Microsyst. 3, 429 (2004)
- 10. "Effects of photoresist polymer molecular weight on line-edge roughness and its metrology probed with Monte Carlo simulations", G.P. Patsis, V. Constantoudis, and E. Gogolides, *Microelectronic Engineering* 75(3), 297 (2004)
- 11. "Line edge roughness and critical dimension variation: Fractal characterization and comparison using model functions", V. Constantoudis, G. P. Patsis, L. H. A. Leunissen, and E. Gogolides, *J. Vac. Sci. Technol. B* (22), 1974 (2004), and *Virtual Journal of Nanoscale Science & Technology*-Volume 10, Issue 9 (August 30 2004)
- 12. "Si etching in high-density SF₆ plasmas for microfabrication: Surface roughness formation", E. Gogolides, C. Boukouras, G. Kokkoris, O. Brani, A. Tserepi, V. Constantoudis, *Microelectronic Engineering* 73-74, 312 (2004)
- "Oxygen plasma modification of polyhedral oligomeric silsesquioxane (POSS) containing copolymers for micro and nano fabrication", N. Vourdas, V. Bellas, E. Tegou, O. Brani, V. Constantoudis, P. Argitis, A. Tserepi, E. Gogolides, *Plasma Processing of Polymers*, pp. 281-292, (2004)
- 14. "Simulation of SiO₂ and Si feature etching for microelectronics and MEMS fabrication: a combined simulator coupling modules of surface etching, local flux calculation, and profile evolution", G. Kokkoris, A. Tserepi, A. G. Boudouvis, and E. Goggolides, *J. Vac. Sci. Technol. A* 22, 1896 (2004)
- "Selective Plasma-induced Deposition of Fluorocarbon Films on Metal Surfaces for actuation in microfluidics", P. Bayiati, A. Tserepi, E. Gogolides, K. Misiakos, J. Vac. Sci. Technnol. A 22(4), 1546-1551, (July/August 2004)
- "Nitrogen distribution during oxidation of low and medium energy nitrogen implanted Silicon", Skarlatos D., Perego M., Tsamis C., Ferrari S., Fanciulli M. and Tsoukalas D., Nuclear Instruments and Methods in Physics Research, B 216, p.75-79, (2004)
- "Oxidation of nitrogen implanted silicon: Comparison of nitrogen distribution and electrical properties of oxides formed by very low and medium energy N₂⁺ implantation", Skarlatos D., Kapetanakis E., Normand P., Tsamis C., Perego M., Ferrari S., Fanciulli M. and Tsoukalas D., *Journal Of Appl. Physics*, 96 (1), p. 300-309 (2004)
- Comparison of FTIR transmission spectra of thermally and LPCVD grown by TEOS pyrolysis, SiO₂ films Vassilis Em. Vamvakas and D. Davazoglou. *Journal of the Electrochemical Society* Vol. 151, 93 (2004)
- "Fabrication of very fine copper lines on silicon substrates patterned with PMMA via selective chemical vapor deposition" D. Davazoglou, I Raptis, A. Gleizes and M. Vasilopoulou Journal of Vacuum Science and Technology B Vol. 22, 859 (2004)
- "Optical properties of SiO₂-TiO₂ sol-gel thin films" P. Chrysicopoulou, D. Davazoglou, C. Trapalis and G. Kordas Journal of Materials Science 39 (8): 2835-2839 (2004)
- 21. "Silicon nanocrystals in SiO₂ thin layers", Nassiopoulou A. G., *Encyclopedia of Nanoscience and Nanotechnology*, edited by H. S. Nalwa, vol. 9 p. 793-813 (2004)
- "Selective self-alignment of Au nanoparticle-coated K₂SO₄ microcrystals in micrometer gratings of V-grooves on a silicon substrate", Nassiopoulou A. G., Zoy A., Ioannou-Sougleridis V., Olzierski A., Travlos A., Martinez-Albertos J. L. and Moore B., *Nanotechnology* 15, 1-5, 352-356, (2004)
- "Growth of two-dimensional arrays of silicon nanocrystals in thin SiO₂ layers by low pressure chemical vapour deposition and high temperature annealing/oxidation. Investigation of their charging properties", Salonidou A., Nassiopoulou A. G., Travlos A., Ioannou-Sougleridis V. and Tsoi E., *Nanotechnology* 15, 1-7, 1233-1239, (2004)
- "Transient and ac electrical transport under forward and reverse bias conditions in aluminium/ porous silicon/p-cSi structures", Theodoropoulou M., Karahaliou P. K., Krontiras C. A., Georga S. N., Xanthopoulos N., Tsamis C. and Nassiopoulou A. G., J. Appl. Phys. 96, 12, (2004)
- 25. "Influence of magnetic field on electromagnetic instabilities in Semiconductor superlattices", Tarkhanyan R. H. and Nassiopoulou A. G., *J. Nanosci. Nanotech.* 4, 1085, (2004)

- "Two-dimensional arrays of nanometer scale holes and nano-V-grooves in oxidized Si wafers for the selective growth of Ge dots or Ge/Si hetero-nanocrystals", Olzierski A., Nassiopoulou A. G., Raptis I. and Stoica T., *Nanotechnology* 15, 1695-1700 (2004)
- 27. "Transient and ac conductivity of nanocrystalline porous alumina thin films on silicon, with embedded silicon nanocrystals" J. of Applied Physics, 95,5, 2776-2780 (2004)
- "Nanocrystals manufacturing by ultra-low-energy ion-beam-synthesis for nonvolatile memory applications", P. Normand, E. Kapetanakis, P. Dimitrakis, D. Skarlatos, K. Beltsios, D. Tsoukalas, C. Bonafos, G. Ben Asssayag, N. Cherkashin, A. Claverie, J. A. Van Den Berg, V. Soncini, A. Agarwal, M. Ameen, M. Perego, M. Fanciulli, *Nucl. Instr. Meth. Phys. Res. B (NIMB)* 216, 228-238 (2004)
- "Silicon nanocrystal memory devices obtained by ultra-low-energy ion-beam-synthesis", P. Dimitrakis, E. Kapetanakis, D. Tsoukalas, D. Skarlatos, C. Bonafos, G. Ben Asssayag, A. Claverie, M. Perego, M. Fanciulli, V. Soncini, R. Sotgiu, A. Agarwal, M. Ameen, P. Normand, *Solid State Electronics* 48, 1511-1517 (2004)
- "Manipulation of two-dimensional arrays of Si nanocrystals embedded in thin SiO₂ layers by low energy ion implantation", C. Bonafos, M. Carrada, N. Cherkashin, H. Coffin, D. Chassaing, G. Ben Assayag, A. Claverie, T. Muller and K. H. Heinig, M. Perego and M. Fanciulli, P. Dimitrakis, P. Normand, J. Appl. Phys. 95, 5696-5702 (2004)
- 31. "Size and aerial density distributions of Ge nanocrystals in a SiO₂ layer produced by molecular beam epitaxy and rapid thermal processing", A. Kanjilal, J. Lundsgaard Hansen, P. Gaiduk, A. Nylandsted Larsen, P. Normand, P. Dimitrakis, D. Tsoukalas, N. Cherkashin, A. Claverie, *Appl. Phys. A Mater. Sc. Process. Online* (June 2004)
- 32. "Processing issues in silicon nanocrystal manufacturing by ultra-low-energy ion-beam-synthesis for non-volatile memory applications", P. Normand, P. Dimitrakis, E. Kapetanakis, D. Skarlatos, K. Beltsios, D. Tsoukalas, C. Bonafos, H. Coffin, G. Benassayag, A. Claverie, V. Soncini, A. Agarwal, Ch. Sohl, M. Ameen, *Microelectronic Engineering* 73-74, 730-735 (2004)
- "Integration of organic insulator and self-assembled gold nanoparticles on Si MOSFET for non-volatile memory cells", S. Kolliopoulou, P. Dimitrakis, P. Normand, H-L. Zhang, N. Cant, S. D. Evans, S. Paul, C. Pearson, A. Molloy, M. C. Petty, D. Tsoukalas, *Microelectronic Engineering* 73-74, 725-729 (2004)
- "Tunneling and negative resistance effects for composite materials containing polyoxometalate molecules"G. Chaidogiannos, D. Velessiotis, P. Argitis, P. Koutsolelos, C. D. Diakoumakos, D. Tsamakis and N. Glezos, *Microel. Eng.* 73-74, 746 (2004)
- "Capacitive Type Chemical Sensors Using Thin Silicon/Polymer Bimorph Membranes", S. Chatzandroulis, E. Tegou, D. Goustouridis, S. Polymenakos, D. Tsoukalas, Sensors and Actuators B: Chemical, Volume 103, Issues 1-2, Pages 392-396, (29 September 2004)
- 36. "Fabrication of Chemical Sensors based on Si/polymer bimorphs", S. Chatzandroulis, E. Tegou, D. Goustouridis, S. Polymenakos, D. Tsoukalas, *Microelectronic Engineering, Volumes 73-74, Pages 847-851* (June 2004)
- "Characterization of Polymer Layers for Silicon Micromachined Bilayer Chemical Sensors Using White Light Interferometry", D. Goustouridis, K. Manoli, S. Chatzandroulis, M. Sanopoulou, I. Raptis accepted for publication in Sensors and Actuators B
- "The influence of thermal treatment on the stress characteristics of suspended Porous Silicon membranes on silicon", D. Papadimitriou, C. Tsamis and A. G. Nassiopoulou, Sensors and Actuators B: Chemical, Volume 103, Issues 1-2, Pages 356-361 (2004)
- 39. "Protein patterning by micromachined silicon embossing on polymer surfaces", Goustouridis D, Misiakos K, Petrou P S, Kakabakos S E, *Applied Physics Letters 85* (26): 6418-6420 (December 27 2004)
- "Selective plasma-induced deposition of fluorocarbon films on metal surfaces for actuation in microfluidics", Bayiati P, Tserepi A, Gogolides E, Misiakos K, *Journal Of Vacuum Science & Technology A* 22 (4): 1546-1551 (Jul-Aug 2004)
- 41. "A monolithic silicon optoelectronic transducer as a real-time affinity biosensor", Misiakos K, Kakabakos S E, Petrou P S, Ruf H H, *Analytical Chemistry* 76 (5): 1366-1373 (Mar 1 2004)
- 42. "Effects of hot carrier and irradiation stresses on advanced excimer laser annealed polycrystalline silicon thin film transistors", Kouvatsos, D. N., Davidovic V., Papaioannou G. J., Stojadinovic N., Michalas L., Exarchos M., Voutsas A. T. and Goustouridis D., *Microelectronics Reliability* 44 (9-11), 1631, (September 2004)
- 43. "Low temperature wafer bonding for thin silicon film transfer", D. Goustouridis, K. Minoglou, S. Kolliopoulou, S. Chatzandroulis, P. Morfouli, P.Normand and D. Tsoukalas, *Sensors and Actuators A: Physical* Volume 110, Issues 1-3, 401-406, (February 2004)
- 44. "A compact non-linear equivalent circuit model and parameter extraction method for packaged high-speed VCSELs", K. Minoglou, E. D. Kyriakis-Bitzaros, D. Syvridis, G. Halkias, *IEEE Journal of Lightwave Technology*, Vol.22, No.12, pp.2823-2827, (December 2004)

B. PUBLICATION IN CONFERENCE PROCEEDINGS

- 1. "Material origins of line-edge roughness: Monte Carlo simulations and scaling analysis", G. P. Patsis, V. Constantoudis, and E. Gogolides, Proc. *SPIE Int. Soc. Opt. Eng.* 5376, 773 (2004) (Poster)
- "Toward a complete description of linewidth roughness: a comparison of different methods for vertical and spatial LER and LWR analysis and CD variation", V. Constantoudis, G. P. Patsis, L. H. A. Leunissen, and E. Gogolides, Proc. SPIE Int. Soc. Opt. Eng. 5375, 967 (2004) (Poster)
- "Effects of different processing conditions on line-edge roughness for 193-nm and 157-nm resists", M. Ercken, L. H. A. Leunissen, I. Pollentier, G. P. Patsis, V. Constantoudis, and E. Gogolides, Proc. SPIE Int. Soc. Opt. Eng. 5375, 266 (2004) (Poster)
- "Increased plasma etch resistance of thin polymeric and photoresist films", N. Vourdas, E. Gogolides, A.G. Boudouvis, *Proceedings of Micro & Nano Engineering (MNE)* 2004, Rotterdam-Netherlands, 19-22 September 2004

- "Characterization of the roughness of structures and surfaces through SEM and AFM images", V. Constantoudis, G.P. Patsis, E. Gogolides, A. Tserepi, E. Valamontes, and O. Brani, *Proceedings of the XIX Panhelenic Conference* of Solid State and Materials Science, 2004 (in Greek)
- 6. "Modification of the morphology of Si-contained polymer surfaces after plasma treatment", A. Tserepi V. Constantoudis, G. Cordoyiannis, E. Valamontes, N. Vourdas and E. Gogolides, *Proceedings of the XIX Panhelenic Conference of Solid State and Materials Science*, 2004 (in Greek)
- "Manipulation of 2D-Arrays of Si Nanocrystals Embedded in a Thin SiO₂ Layer by Low Energy Implantation", C. Bonafos, G. Ben Assayag, S. Schamm, H. Coffin, N. Cherkashin, A. Claverie, P. Normand, P. Dimitrakis, M. Perego, M. Fanciulli, T. Mueller, K-H. Heinig, M. Tence, C. Colliex, Oral presentation, *Materials Research Society Fall Meeting 2004, MRS Fall 04*, Symposium D, Boston, USA, November 29 December 3 (2004)
- "Ge Nanocrystals in MOS-Memory Structures Produced by Molecular-Beam Epitaxy and Rapid-Thermal Processing", A. Nylandsted Larsen, A. Kanjilal, J. L. Hansen, P. Gaiduk, P. Normand, P. Dimitrakis, D. Tsoukalas, N. Cherkashin, A. Claverie, Poster presentation, *Materials Research Society Fall Meeting 2004, MRS Fall 04, Symposium D*, Boston, USA, November 29 - December 3 (2004)
- "Oxidation of Si nanocrystals obtained by low energy ion implantation in a thin SiO₂ layer", H. Coffin, C. Bonafos, N. Cherkashin, S. Schamm, G. Ben Assayag, G. Zanchi, P. Dimitrakis, P. Normand, M. Tence, C. Colliex, A. Claverie, Poster presentation, *Materials Research Society Fall Meeting 2004, MRS Fall 04, Symposium D*, Boston, USA, November 29 - December 3 (2004)
- "Gold Langmuir-Blodgett deposited nanoparticles for non-volatile memories", P. Dimitrakis, S. Kolliopoulou, D. Tsoukalas, P. Normand, S. Paul, C. Pearson, A. Molloy, M. C. Petty, Poster presentation, *Materials Research Society Fall Meeting 2004, MRS Fall 04, Symposium D*, Boston, USA, November 29 December 3 (2004)
- 11. "A Si/SiGe MOSFET utilizing low-temperature wafer bonding", S. Kolliopoulou, P. Dimitrakis, D. Goustouridis, S. Chatzandroulis, P. Normand, D. Tsoukalas, H. Radamson, Poster presentation, *International Conference on Microand Nano-Engineering, MNE04*, Rotterdam, Netherlands, September 19-22 (2004)
- 12. "Single electron charging mechanisms into silicon quantum dots realized by ultra low energy implantation", Oral presentation, A. Beaumont, P. Normand, G. Ben Assayag, A. Claverie, A. Souifi, *European Materials Research Society Conference, E-MRS04*, Strasbourg, France, June (2004)
- "Poly [(ethylenedioxy) thiophene] conductive films", M. Biler, L. T. D. Dvorakova, S. Nespurek and N. Glezos, World Polymer Conference, 40th Symposium on Macromolecules, Paris 2004
- 14. "Quantum effects in molecular nanodevices based on tungsten polyoxometalates", D.Velessiotis, G.Chaidogiannos, N.Glezos and P.Argitis, *European Microelectronics and Packaging Symposium, Prague* 2004
- "An investigation of the electrically active defects in poly-Si thin film transistors", Exarchos, M., Papaioannou G. J., Kouvatsos D. N. and Voutsas A. T., *Thin Film Transistor Technologies VII Symposium Proceedings*, 206th Meeting of the Electrochemical Society, Honolulu, Hawaii, (October 2004)
- 16. "Effects of Packaging Parasitics on High Speed operation of VCSELs", K. Minoglou, E. D. Kyriakis-Bitzaros, A. Arapoyanni and G. Halkias, *NEWCAS 2004*, pp.53-56 20-23 June 2004, Montreal, Canada
- 17. "Development of a new parameter extraction methodology for the modeling of the input of the VCSELs", K.Minoglou, E. D. Kyriakis-Bitzaros, D. Syvridis, G. Halkias, *HETECH 2004, 13th European Workshop on Heterostructure Technology*, October 3-6, 2004, Heraklion, Crete, Greece

C. PRESENTATIONS in CONFERENCES

- "Sub 10 μm Protein Microarrays Fabricated Using New Near UV Photoresist and Novel Multi-Step Lithographic Scheme", M. Chatzichristidi, A. Douvas, K. Misiakos, I. Raptis, C.D. Diakoumakos, P. Petrou, S. E. Kakabakos, P. Argitis, 2nd International Workshop on Multi-Analyte Biosensing Devices, Tarragona, Spain, 18-19 of February 2004
- "157 nm laser ablation of polymeric layers for fabrication of biomolecule microarrays", P. Petrou, A. Douvas, S. E. Kakabakos, P. Argitis, K. Misiakos, E. Sarantopoulou, Z. Kollia, A. C. Cefalas, 2nd International Workshop on Multi-Analyte Biosensing Devices, Tarragona, Spain, (18-19 February 2004)
- "Fabrication of Microscale Protein Arrays for Low Crosstalk Electrochemical Sensing", Bush, I. Katakis, M. Chatzichristidi, K. Misiakos, P. Argitis, 2nd International Workshop on Multi-Analyte Biosensing Devices, Tarragona, Spain, (18-19 February 2004)
- "Dissolution properties of ultrathin photoresist films for the fabrication of nanostructures", A. Kokkinis, E. S. Valamontes, I. Raptis, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Characterization of various low-k dielectrics for possible use in applications at temperatures below 160°C", M. Vasilopoulou, S. Tsevas, A. M. Douvas, P. Argitis, D. Davazoglou and D. Kouvatsos, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Photochemically Induced Emission Tuning of Conductive Polumers used in OLEDs", M. Vasilopoulou, G. Pistolis and P. Argitis, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Line Width Roughness (LWR) metrology, characterization, and simulation: Developing the software tools for understanding, describing, and predicting LER", E. Gogolides, V. Constantoudis, G. P. Patsis, *EUVL Workshop* 2004, Roterdam, 23/9/04 (Poster)
- 8. "Calculations of electron-beam energy deposition in resist films over multiplayer Si/Mo substrates", G. P. Patsis, N. Glezos, *Microfabrication, Microsystems and Nanotechnology (MNN)*, Athens, 2004. (Talk)
- 9. "Effects of polymer chain architecture on film surface and line edge roughness. Monte Carlo Simulations", G. P. Patsis, and E. Gogolides, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece (Poster)

- "Plasma etch rate measurements of thin PMMA films correlation with the glass transition temperature", N. Vourdas, A. G. Boudouvis, E. Gogolides, 2nd Conference on Microelectronics, Microsystems and Nanotechnology (MMN2004), Athens, Greece, November 15-17, 2004
- "Patterning of thick polymeric substrates for the fabrication of micrifluidic devices", M.E. Vlachopoulou, A. Tserepi, N. Vourdas, E. Gogolides and K. Misiakos, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Electrowetting of plasma-deposited hydrophobic films as a means for fluid transport in microfluidics", A. Tserepi, P. Bayiati, K. Misiakos, E. Gogolides, 4th Int. Meeting on Electrowetting, Blaubeuren, Sept. 2004 (poster)
- "Complexity in Science and Society" Patras, July 2004 (poster: "Fractal structures in nanoelectronics") (best poster award)
- 14. "Fractal polymer surfaces after lithographic processing", XX Panhelenic Conference on Solid State and Materials Science, Ioannina September 2004
- "Profile evolution during SiO₂ and deep Si feature etching", G. Kokkoris, A. G. Boudouvis, and E. Gogolides, 16th International Vacuum Congress, Venice, Italy, June 28 - July 2, 2004
- 16. "Formation and characterization of ultrathin oxides formed by oxidation of very low energy nitrogen implanted silicon", Skarlatos D., Kapetanakis E., Normand P., Tsamis C., Tsoukalas D., Perego M, Ferrari S., Fanciulli M. and Stoemenos J., 13th MEL ARI NID Workshop, 4-6 February 2004, Athens, Greece (poster presentation)
- "Point defect injection during diffusion of low energy As-implanted silicon", Tsamis C., Skarlatos D., Tsoukalas D., Ben-Assayag G., Claverie A. and Lerch W, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece (poster presentation)
- "FORUM FIB: Fabrication organization and use of memories obtained by Focused Ion Beam", I. Berbezier, A. Karmous, A. Ronda, T. Stoica, R. Geurt and A.G. Nassiopoulou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Ultrafast carrier dynamics in highly implanted and annealed polycrystalline silicon films", E. Lioudakis, A. Othonos and A.G. Nassiopoulou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Nanotemplate alumina films on a silicon substrate fabricated by electrochemistry", M.Kokonou, A. G. Nassiopoulou, K. P. Giannakopoulos and N. Boukos, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Generation of guided terahertz electromagnetic waves in semiconductor superlattices", R.H.Tarkhanyan and A.G. Nassiopoulou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Investigation of electronic conductivity of nanoparticle coated microcrystals", A. Zoy, A. G. Nassiopoulou, M. Murugesan and B. Moore, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece (to appear in J. of Phys. Conf. Series)
- 23. "Influence of near interface oxide traps on the charging characteristics of Si nanocrystals embedded within SiO₂", V. Ioannou-Sougleridis and A. G. Nassiopoulou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 24. "Silicon nanocrystal memory cells by low pressure chemical vapor deposition of amorphous silicon on SiO₂ and oxidation", E. Tsoi, P. Normand, A. G. Nassiopoulou, V. Ioannou-Sougleridis and A. Salonidou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 25. "Density of interface traps in ultra thin porous anodic alumina films on silicon", M. Theodoropoulou, P.K. Karahaliou, S.N. Georga, C.A. Krontiras, M.N. Pisanias, M. Kokonou and A.G. Nassiopoulou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 26. "Ordered 2-D arrays of Ge quantum dots embedded in ultra thin SiO₂", A. Olzierski, A. G. Nassiopoulou and A. Travlos, *EMRS 2004*, Strasbourg, France
- "Very thin anodic alumina films with ordered pore arrays on a silicon substrate", M. Kokonou, A. G. Nassiopoulou and K. P. Giannakopoulos, *International Conference on Porous Semiconductor Science and Technology*, Valencia, Spain, (March 14-19, 2004)
- 28. "Photoluminescence of very thin anodic alumina films on a silicon substrate", M. Kokonou and A.G. Nassiopoulou, *International Conference on Porous Semiconductor Science and Technology*, Valencia, Spain, (March 14-19, 2004)
- "2-D arrays of Ge quantum dots in SiO₂ for non-volatile memories", A. Olzierski, A. Nassiopoulou, A. Travlos, T. Stoica, XX Panhellinion Conference on Solid State Physics and Materials Science, Ioannina (26-29 September, 2004)
- "Porous alumina thin films on Si with self-assembled vertical pores", M. Kokonou, A. G. Nassiopoulou and K. P. Giannakopoulos, XX Panhellinion Conference on Solid State Physics and Materials Science, Ioannina, (26-29 September, 2004)
- "Study of interface state density in porous alumina/c-Si MOS structures", M. Theodoropoulou, P. Karachaliou, S. N. Georga, C. Krontiras, M. Pizanias, M. Kokonou and A. G. Nassiopoulou, XX Panhellinion Conference on Solid State Physics and Materials Science, Ioannina, (26-29 September, 2004)
- 32. "Memory devices obtained by Si⁺ irradiation through poly-Si/SiO₂ gate stack", P. Dimitrakis, P. Normand, E. Votintseva, K-H. Stegemann, K-H. Heinig, B. Schmidt, Oral presentation, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 33. "Field effect devices with metal nanoparticles integrated by Langmuir-Blodgett technique for non-volatile memory applications", S. Kolliopoulou, D. Tsoukalas, P.Dimitrakis, P. Normand, S. Paul, C. Pearson, A. Molloy, M. C. Petty, Poster presentation, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece

- 34. "Compound polymeric materials in molecular nanodevices: Electrical behavior of zero-dimension semiconducting inorganic molecules embedded in a polymer substrate", D Velessiotis, V Ioannou-Sougleridis, G Chaidogiannos and N Glezos, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 35. "Combination of integrated thermal flow and capacitive pressure sensors for high sensitivity flow measurements in both laminar and turbulent regions", G. Kaltsas, D. Goustouridis, A. G. Nassiopoulou and D. Tsoukalas, *Journal of Physics*: Conference Series (accepted for publication), 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 36. "A microcontroller-based interface circuit for data acquisition and control of a micromechanical thermal flowsensor", P. Asimakopoulos, G. Kaltsas and A. G. Nasisopoulou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece, To appear in Journal of Physics: Conference Series
- 37. "Simultaneous use of flow and pressure sensors for flow determination in both laminar and turbulent regions", G. Kaltsas, D. Goustouridis, A. G. Nassiopoulou and D. Tsoukalas, *International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004)*, November 14-17, Athens, Greece
- "Investigation of different operation modes of a micromechanical thermal flow sensor, using a microcontrollerbased interface circuit", P. Asimakopoulos, G. Kaltsas and A. G. Nassiopoulou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Stress characteristics of suspended Porous Silicon microstructures on silicon", K. Anestou, D. Papadimitriou, C. Tsamis and A.G. Nassiopoulou, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 40. "A CMOS compatible thermal accelerometer without solid proof mass, based on porous silicon thermal isolation", G. Kaltsas, D. Goustouridis and A. G. Nassiopoulou, *IEEE Sensors 2004*, Vienna, Austria, October 24-27, 2004
- 41. "A CMOS compatible process for porous silicon/air cavity formation for application in thermal sensors and microfluidic devices", D. N. Pagonis, A. G. Nassiopoulou and G. Kaltsas, 4th Int. Con. 4th Int. Con. On Porous Semiconductors Science and Technology (PSST 2004), Cullera-Valencia, Spain, March 14-19, 2004
- 42. "Porous silicon micro-hotplates for low power thermal sensors. Measurements at reduced pressures and estimation of porous silicon thermal conductivity of porous silicon", C. Tsamis, K. Spyropoulos and A. G. Nassiopoulou, 4th Int. Con. On Porous Semiconductors Science and Technology (PSST 2004), Cullera-Valencia, Spain, March 14-19, 2004
- 43. "Fabrication and characterization of an integrated thermal flow sensor using porous silicon membranes over cavity for local thermal isolation", D. N. Pagonis, A.G. Nassiopoulou and G. Kaltsas, applied to the XX Panhellinion Conference on Solid State Physics and Materials Science26-29 September, Ioannina 2004
- 44. "Characterization of Polymer Layers for Silicon Micromachined Bilayer Chemical Sensors Using White Light Interferometry", D. Goustouridis, S. Chatzandroulis, M. Sanopoulou, I. Raptis, *EUROSENSORS XVIII, September* 13-15, 2004 Italy Rome
- 45. "Polymeric film characterization for use in Bimorph Chemical Sensors", S. Chatzandroulis, D. Goustouridis, I. Raptis, *Micro- and Nano-Engineering (MNE) 2004, Rotterdam, The Netherlands, September 19 22*
- 46. "Modification Of Polymer Swelling By UV Irradiation For Use In Chemical Sensing", D. Goustouridis, S. Chatzandroulis, I. Raptis, E. S. Valamontes, *IEEE SENSORS 3rd Int. Conference on Sensors, Vienna, Austria, Oct.* 24-27, 2004
- 47. "Simulation of Capacitive type Bimorph Humidity Sensors", J. Fragakis, S. Chatzandroulis, D. Papadimitriou, C. Tsamis, "MMN 2004, 15-17 November 2004 Athens, Greece
- 48. "Polymeric film characterization for use in bimorph chemical sensors", S. Chatzandroulis, D. Goustouridis, I. Raptis, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 49. "Porous silicon micro-hotplates for low power thermal sensors. Measurements at reduced pressures and estimation of porous silicon thermal conductivity", C. Tsamis, K. Spyropoulou and A. G. Nassiopoulou, *Fourth International Conference on "Porous Silicon Science and Technology", PSST 2004, March 2004, Valencia, Spain (Oral presentation)*
- "Stress characteristics of suspended Porous Silicon microstructures on silicon"K. Anestou, D. Papadimitriou, C. Tsamis and A. G. Nassiopoulou, 2nd Conference on Microelectronics, Microsystems, Nanotechnology, MMN 2004, 15-17 November 2004, Athens, Greece (Poster presentation)
- 51. "A bioanalytical microsystem for protein and DNA sensing based on a monolithic silicon optoelectronic transducer", K. Misiakos, P.S. Petrou, S.E. Kakabakos, H. H. Ruf, T. Knoll, E. Ehrentreich-Foerster and F.F. Bier, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 52. "New lithographic process and resist capable for fabrication of submicron protein microarrays", Chatzichristidi M., Douvas A., Misiakos K., Raptis I., Diakoumakos C. D., Argitis P., Petrou P. S. and Kakabakos S.E, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 53. "The effect of Generation-Recombination mechanisms on the transient behavior of polycrystalline silicon transistors", Papaioannou G.J., Voutsas A., Exarchos M. and Kouvatsos D., δth International Conference on Polycrystalline Semiconductors Materials, Technologies and Device Applications, Potsdam, Germany, (September 2004)
- 54. "Effects of hot carrier and irradiation stresses on advanced excimer laser annealed polycrystalline silicon thin film transistors", Kouvatsos, D. N., Davidovic V., Papaioannou G. J., Stojadinovic N., Michalas L., Exarchos M., Voutsas A.T. and Goustouridis D., 15th European Symposium Reliability of Electron Devices, Failure Physics and Analysis (ESREF 2004), Zurich, Switzerland, (October 2004)

- 55. "Effects of DC gate and drain bias stresses on the degradation of excimer laser crystallized polysilicon thin film transistors", Kouvatsos, D. N., Michalas L., Voutsas A. T. and Papaioannou G. J., 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- 56. "Investigation of drain current transient behavior in SLS TFTs with the DLTS technique", Exarchos M. A., Papaioannou G. J., Kouvatsos D. N. and Voutsas A. T., 2nd Conference on Microelectronics, Microsystems and Nanotechnology, Athens, Greece, (November 2004)
- 57. "Metallic bonding of optoelectronic dies to silicon wafers", K. Minoglou, E. D. Kyriakis-Bitzaros, E. Grivas, S. Katsafouros, A. Kostopoulos, G. Konstadinidis and G. Halkias, 2nd International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004), November 14-17, Athens, Greece
- "Laser ablation of polymeric layers for fabrication of biomolecule microarrays" P. S. Petrou, A. Douvas, S. E. Kakabakos, K. Misiakos, P. Argitis, E. Sarantopoulou, Z. Kollia and C. Cefalas, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 33
- 59. "Sub-10 μm protein microarrays fabricated using new near UV photoresist and novel multi-step lithographic scheme", M. Chatzichristidi, A. Douvas, K. Misiakos, I. Raptis, C. D. Diakoumakos, P. Petrou, S. E. Kakabakos and P. Argitis, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 32
- 60. "Printing protein patterns". K. Misiakos, D. Goustouridis, S. Kakabakos, P. Petrou. 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 38
- "Multianalyte integrated optical biosensors based on monolithic silicon optoelectronic transducers" K. Misiakos, S. Kakabakos, P. Petrou and H. Ruf, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 60
- "Development of a capillary-based fluoroimmunosensor capable for real-time measurement of the analytical signal", C. Mastichiadis, S. E. Kakabakos, P. S. Petrou, I. Christofidis and K. Misiakos, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 70
- 63. "Fabrication of microscale protein arrays for low crosstalk electrochemical sensing", A. Bush, I. Katakis, M. Chatzichristidi, K. Misiakos and P. Argitis, 2nd International Workshop on Multi-analyte Biosensing Devices, Tarragona, Spain, 18-20 February, 2004, Abstract p. 36
- 64. "Plasma-deposited fluorocarbon films for use in actuation of fluid movement in microfluidic devices", Bayiati P., Tserepi A, Gogolides E, Misiakos K, Abstract p. 67
- 65. "Characterization of Advanced Excimer Laser Crystallized Polysilicon Thin Film Transistors", Exarchos M., Kouvatsos D. N., Papaioannou G. J., Davidovic V., Stojadinovic N., Michalas L., and Voutsas A. T., Proceedings of the 24th International IEEE Conference on Microelectronics (MIEL 2004), Nis, Yugoslavia, (May 2004)
- 66. "Wheeler's law and related issues in Integrated Antennas", H. Contopanagos, S. Rowson and L. Desclos, published in 2004 IEEE Antennas & Propagation Society International Symposium Digest, (June 20-26,2004, Monterey, CA).
- "Electromagnetic design methods in systems-on-chip: Integrated filters for wireless CMOS RFICs" H. Contopanagos, to appear in *Journal of Physics: Conference Series*, International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004, November 14-17, Athens, Greece).

INVITED TALKS

- 1. "Determining the impact of statistical fluctuations on resist line-edge roughness", L.H.A. Leunissen, M. Ercken, G. P. Patsis, **Invited talk**, *Micro and Nanoengineering (MNE)*, Roterdam (2004)
- 2. "Low dimensional Si or Ge for application in nanodevices", A. G. Nassiopoulou, **Invited talk**, *International Workshop on ultimate Lithography and Nanodevice Engineering*, Agelonde, France, 13-16 June 2004
- 3. "2-D arrays of Semiconductor nanocrystals in thin SiO2 layers application in quantum dot memories", A. G. Nassiopoulou, **Invited talk**, *E-MRS spring Meeting Symposium I*, (May 24-28, 2004)
- 4. "Low-dimensional Si for optoelectronics and memory devices, A. G. Nassiopoulou, **Invited talk**, *NATO Advanced Study Institute on Nanostructured and Advanced Materials for Optoelectronic, Photovoltaic & Sensor applications*, Sozopol, Bulgaria, (September 6-17, 2004)
- "Semiconductor nanocrystal floating-gate memory devices", P. Dimitrakis and P. Normand, Invited talk, Materials Research Society Fall Meeting 2004, MRS Fall 04, Symposium D, Boston, USA, (November 29 - December 3, 2004)
- 6. "Nanocrystal memory for future electronics", P. Normand, **Invited talk**, 13th European Workshop on Heterostructure Technology, HETECH 2004, Heraklion, Greece, (October 3-6, 2004)
- "Porous silicon for sensor applications", A. G. Nassiopoulou, Invited talk, NATO Advanced Study Institute on Nanostructured and Advanced Materials for Optoelectronic, Photovoltaic & Sensor applications, Sozopol, Bulgaria, (September 6-17, 2004)
- "Electromagnetic design methods in systems-on-chip: Integrated filters for wireless CMOS RFICs", H. Contopanagos, Invited talk, International Conference on Microelectronics, Microsystems and Nanotechnology (MMN 2004, November 14-17, Athens, Greece).

ANNEX III: RESEARCH PROJECTS RUNNING IN 2004

A. EU Projects

- ♦ GROWTH SAFEGAS Contract Nº G1RD-1999-00167 "Sensor array for fast explosion proof gas monitoring" Duration: 1/1/01-30/6/04 Responsible: A. Nassiopoulou
- IST FET FRACTURE Contract Nº 26014
 "Nanoelectronic Devices and Fault-Tolerant Architectures" Duration: 1/1/2001 - 30/3/2004 Responsible: D. Tsoukalas
- ◆ GROWTH MATERIALS NEON Contract N° 25619
 "Nanoparticles for Electronic applications"
 Duration: 1/2/01 30/12/04
 Responsible: P. Normand
- IST FORUM FIB Contract N° 29573
 "Fabrication, organization and use of memories obtained by FIB" Duration: 1/7/2001 - 30/6/2004 Responsible: A. Nassiopoulou
- ◆ IST BIOMIC Contract N° 28214
 "A Bioanalytical Microsystem Based on an Optical Microchip" (BIOMIC) Duration: 1/6/2001 - 31/5/2004 Responsible: K. Misiakos
- IST 157 CRISPIES Contract Nº 30143
 "Critical Resist and Processing Issus at 157nm Lithography addressing the 70nm node" Duration: 1/10/2001 - 30/9/2004 Responsible: E. Gogolides
- GROWTH MICROPROTEIN G5RD-CT-00744
 "Micrometer Scale Patterning of Protein and Dna Chips" Duration: 1/5/2002 - 31/10/2005 Responsible: P. Argitis
- IST FRENDTECH Contract N° 30129
 "Front-end technology simulation, Information Society Technologies" Duration: 1/9/01-31/8/04 Responsible: D. Tsamis
- IST SOARING Contract N° 35254
 "Development and Validation of Source, Optics and Resist in Next Generation EUV Lithography" Duration: 1/3/02-28/2/05 Responsible: E. Goggolides
- IST ESCHER Contract Nº 33287
 "Self-assembled building blocks for nanocomputers" Duration: 1/1/02-31/12/04 Responsible: A. Nassiopoulou
- ENERGY Contract N° ENK6-CT-2002-00674
 "PROTEAS PV System" Duration: 1/1/2003-31/12/2005 Responsible: D. Davazoglou
- SINANO Contract Nº 506844
 "Silicon based Nanodevices" Duration: 1/1/2004-31/12/2006 Responsible: A. Nassiopoulou

- ♦ GOOD-FOOD Contract N° 508774
 "Food Safety and Quality Monitoring with Microsystems" Duration: 1/1/2004-30/6/2007 Responsible: C. Tsamis
- PICMOS Contract N° 002131
 "Photonic Interconnet Layer on CMOS by Wafer-Scale Integration" Duration: 1/1/2004-31/12/2006 Responsible: G. Halkias
- MORE-MOORE Contract N° 507754 "Exploring new limits to Moore's law" Duration: 1/1/2004-31/12/2006 Responsible: E. Goggolides
- ESA Contract Nº 17884
 "Multigigabit optical backplane interconnections" Duration: 5/1/2004-4/7/2005 Responsible: G. Halkias
- UNINANOCUPS NANO2LIFE under Contract N° 500057
 "Unidirectional nanoscale supramuleculawires assembled by photo and electro-active metallocyclodextrine cups" Duration: 1/1/2004-31/12/2007 Responsible: N. Glezos
- NOE NANO2LIFE under Contract N° 500057
 "Unidirectional nanoscale supramuleculawires assembled by photo- and electro-active metallocyclodextrine cups"
 Duration: 1/2/2004-31/1/2008
 Responsible: K. Misiakos
- MINA-EAST Contract Nº 510470
 "Micro and Nanotechnologies going to Eastern Europe throuth Networking" Duration: 1/5/2004-30/4/2006 Responsible: A. Nassiopoulou

B. Other International projects

- NATO "SubHTS"
 "Damage Free Submicron Structures of High Temperature Superconducting Thin Films", (15440/DIE 377)
 Duration: 15/12/2000 15/12/2004
 Responsible: P. Argitis
- Photothermal project (Research agency-Cyprus)
 "Towards a safe hydrogen production: Photothermal analysis at the limits of parts per trillion" Duration: 1/7/2004 - 30/6/2006 Responsible: A. Nassiopoulou

C. Bilateral projects

- Bilateral project (Greece-Yugoslavia)
 "Fabrication and reliability characterization of metal oxide silicon (MOS) devices with copper metallization for microelectronic applications", Duration: 17/5/2002-16/5/2004 Responsible: D. Kouvatsos
- Bilateral project (Greece-Ukraine)
 "Nanostructured films based on oxides, intermetallides and polymers on semiconductors for chemical sensors"
 Duration: 26/2/2002-25/2/2004
 Responsible: C. Tsamis

• Bilateral project (Greece-France)

"Chemical vapor deposition (CVD) of copper films for microelectronic applications" Duration: 2/1/2002 - 2/1/2004 Responsible: D. Davazoglou

♦ Bilateral project (Greece -Czech Republic)

"Construction of novel electronic ant optical switches based on quantum transport phenomena in molecular nanostructures" Duration: 29/7/03 - 28/7/2005 Responsible: N. Glezos

- Bilateral project (Greece-Poland)
 "Pattern repication in thin polymeric films with novel lithographic approach" Duration: 29/6/2004 - 29/6/2006 Responsible: I. Raptis
- Bilateral project (Greece-Yugoslavia)
 "Performance, stress degradation and reliability characterization of thin film transistors for the investigation of defects in polycrystalline silicon films"
 Duration: 5/11/2004-5/11/2006
 Responsible: D. Kouvatsos

D. Contracts with Industry

- Contract with Remon Medical (Israel) on pressure sensors development Duration: 1/6/01-31/5/02 (31/12/2006) Contract: "Pressure sensors development" Responsible: D. Tsoukalas (P. Normand)
- Contract with the company INTEL "Mol - EU" Duration: 1/5/03 - 30/4/06, Budget: 450.000 € Responsible: E. Goggolides
- Contract with the company SHARP "Analysis of TFT and gated Hall devices by DLTS method to clarify type and quantify density of defect-states present in the device active-layer" Duration: 1/10/03 - 30/9/05 Responsible: D. Kouvatsos
- Contract with the company PHOTRONICS
 "Simulation tool and theoretical calculation of the proximity correction parameters for the e-beam patterning of EUVL masks"

 Duration: 1/6/04 30/4/06
 Responsible: N. Glezos

E. Projects funded by GSRT

♦ PRAXE

"Fabrication of metallized glass substrates for application in decoration using techniques from microelectronics" Duration: 2/6/03-1/12/04 Responsible: D. Davazoglou

♦ PEPER

"Wireless subscriber connection in advanced public electrocommunication networks implemented with systems on chip (wireless-mile) Duration: 1/1/04-30/6/06 Responsible: S. Katsafouros

ANNEX IV : INFRASTRUCTURE

The infrastructure available at IMEL is unique in Greece and it includes state-of-the art equipment and facilities for both micro and nanofabrication in a clean room area, and for design, modeling, characterization and testing of materials, devices, circuits and systems. A great part of the infrastructure has been funded through competitive projects at National and European level.

The clean room of a total area of $300m^2$ has been fully upgraded in the year 2002.

The infrastructure available at IMEL includes the following:

- II. <u>Silicon processing laboratory in a clean room area of 300 m², equipped with the following:</u>
 - 4 laminar flow chemical benches
 - 7 horizontal hot-wall furnace tubes
 - 2 horizontal LPCVD tubes for nitride, oxide (TEOS), polysilicon
 - 1 horizontal LPCVD tube for LTO
 - Ion Implanter (EATON medium current, 200 KeV)
 - Optical lithography systems (resolution down to 0,6 µm)
 - Electron beam lithography system (resolution 50 nm)
 - Reactive Ion Etcher
 - High Density Plasma Etcher
 - Plasma processing system
 - Metallization equipment (thermal, e-gun evaporation, sputtering)
 - Process inspection equipment



III. Characterization, Testing and Inspection Equipment

- Electrical characterization equipment
 - Karl Suss PA150 semi-automatic probe station
 - Karl Suss manual probe station
 - Micromanipulator probe station
 - -HP measuring systems (4142B, 4084B, 8110A, 700i series, 4140B, 4284, 4192A, 34401, 16500A)
 - Keithley measuring equipment (230, 220, 617, 195A, 6517A)
 - Tektronix 224J Oscilloscope
 - Oxford optistat Cryostat for temperatures in the range 4.2-320 K.
 - Oxford DN cryostat for temperatures in the range 77-500 K
- Optical characterization equipment
 - Multiwavelength Spectroscopic Ellipsometer
 - FTIR system, model Tensor 27 of Bruker
 - Jobin Yvon spectrometer, wavelengths 300-1600 nm
 - Argon Laser
 - Oxford optistat Cryostat, 4.2-320 K
- Morphology, structural characterization
 - Leo 440 SEM

- AFM
- Stylus profilometer model XP-2 of Ambios Technology
- Testing equipment
 - Systems for testing of gas flow, gas, pressure, acceleration and humidity sensors.
- III. Modeling/Simulation Software
 - Process and device modeling software
 - SILVACO Software (Athina, Atlas)
 - Suprem and Pisces
 - Floops and floods
 - Coventorware-software for MEMs modeling and simulation
- IV. VLSI Design Facilities
 - Hardware
 - H-P 9000/ 700
 - SUN Ultra workstations
 - Software from schematic or VHDL to mask layout and verification
 - Cadence
 - Mentor Graphics
 - Synopsis



ANNEX V

ORGANIZATIONAL STRUCTURE OF THE SILICON PROCESSING LABORATORY

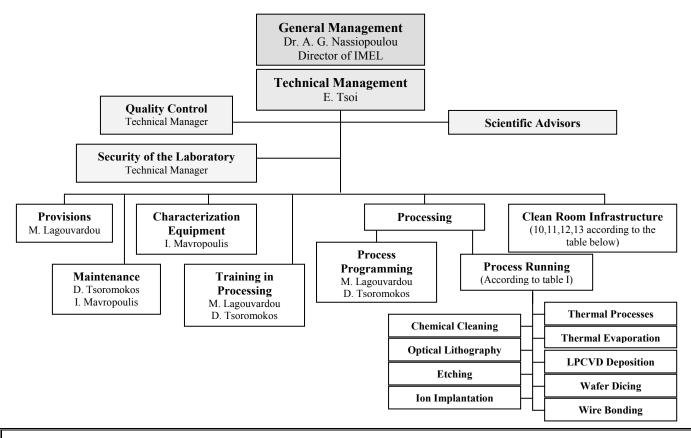


TABLE I

CLEAN ROOM PROCESSES								
	PROCESS	EQUIPMENT	RESPONSIBLE FOR EQUIPMENT	SCIENTIFIC ADVISOR	OPERATORS			
1	Chemical Cleaning	- Chemical benches - Dryer	I. Mavropoulis	E. Tsoi	M. Lagouvardou C. Georgiou D. Tsoromokos			
2	Optical Lithography	 - 3" Mask aligner - 3" and 4" double scale mask aligner - Lithography benches - Spinners - Hot plates 	I. Mavropoulis C. Georgiou	E. Tsoi	M. Lagouvardou C. Georgiou D. Tsoromokos			
3	Etching	Etcher	D. Tsoromokos	E. Gogolides A. Tserepi	D. Tsoromokos E. Bolomiti			
4	Ion Implantation	Ion implanter	D. Tsoromokos	P. Normand	D. Tsoromokos E. Sergis E. Linarakis			
5	Thermal Processes	7 Diffusion furnaces	I. Mavropoulis	E. Tsoi	M. Lagouvardou C. Georgiou D. Tsoromokos			
6	Thin film deposition (Physical Techniques)	Thermal evaporator	E. Sergis	K. Misiakos	E. Sergis M. Lagouvardou D. Tsoromokos			
		e gun evaporator	D. Tsoromokos	K. Misiakos	E. Sergis D. Tsoromokos			
7	LPCVD Deposition	LPCVD deposition (Silicon nitride, TEOS oxide, Polycrystalline silicon, LTO oxide)	E. Sergis	D. Davazoglou	E. Sergis D. Tsoromokos E. Bolomiti			
8	Wafer Dicing	Dicing saw	I. Mavropoulis	E. Tsoi	M. Lagouvardou C. Georgiou			
9	Wire Bonding	Die bonder	I. Mavropoulis	E. Tsoi	C. Georgiou			

Responsibilities

General Manager

General supervision, financing, overall responsibility of access to infrastructure and services

Technical Manager

- Assurance of laboratory running
- Management of processing and laboratory budget
- Security
- Quality system, compatibility of processes with silicon processing

Responsible for Quality Control

- Application of the quality system
- Quality archives
- Control of running processes, compatibility with the quality control system
- Archives of process results
- Tsoi E. Application of security rules
- Training in security rules

Provisions

- Purchase of process consumables and spare parts
- Stocks of chemicals, wafers etc

Responsible for Equipment Maintenance

- Spare parts for the equipment
- Calibration of the equipment

Operators

- Process running
- Calibration of processes
- Standardization, process quality control

Services at European level

Services to other research centers, universities and SMEs are provided by IMEL at the following processes:

- Wafer cleaning
- Thermal processes
- Lithography (optical, e⁻beam)
- Reactive ion and high density plasma etching of nanocrystalline or polycrystalline silicon, silicon oxide and silicon nitride
- Thin film deposition (TEOS and LTO oxide, silicon nitride, polycrystalline silicon, metals)
- Wafer dicing, wire bonding
- Porous silicon formation (patterned areas on a wafer)

A. PERSONNEL TOTAL				
a) Personnel covered by the public budget funding				
- Research scientists and Engineers				
- Post Doctoral Scientists: 6 - PhD Students: 13	19			
- Technicians and Administrative Personnel				
b) Personnel on contract				
- Research Associate (for one year)				
- Post Doctoral Scientists: 3 - PhD Students: 8	11			
- Technicians and Administrative Personnel				
B. RUNNING PROJECTS				
- Competitive EU, GSRT and contracts with industry				
C. RESEARCH OUTPUT				
- Publications in International Journals and Reviews	44			
- Publications in Conference Proceedings (after refereeing), Chapters in Books etc.				
- Presentations in conferences				
- Patents granted in 2004				
- Citations (third party) To papers of IMEL				
- Invited papers				
D. EDUCATION OUTPUT				
- PhD theses carried out at IMEL and completed in 2004				
- Master and Diploma theses carried out at IMEL and completed in 2004				
- Laboratory training of students from Universities	30			

IMEL in figures (Year 2004)