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)

Goals:

- 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

Main results:

a) New resist materials for CMOS processing

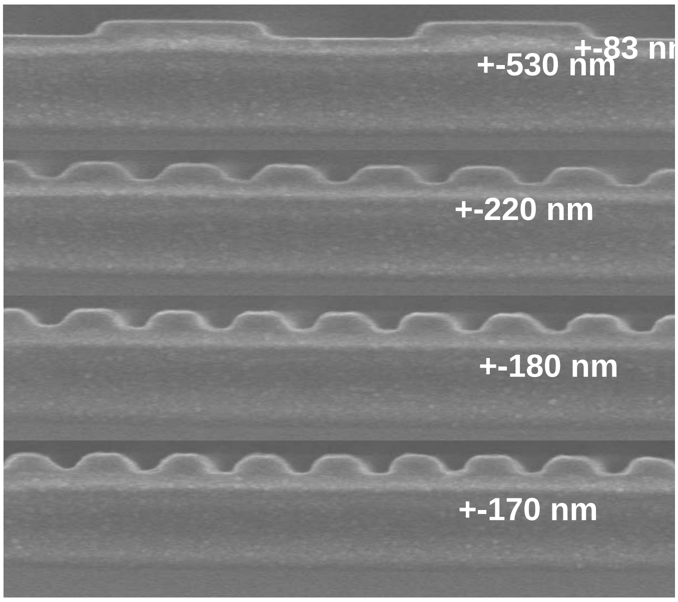
i. Polyhedral Oligomeric Silsesquioxane (POSS) - based resist platform for 193 nm and 157 nm lithography

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. I.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.

<table>
<tr><td>500 µm L/ 500 µm S</td><td rowspan="4">
</td></tr>
<tr><td>150 µm L/ 150 µm S</td></tr>
<tr><td>130 µm L/ 130 µm S</td></tr>
<tr><td>120 µm L/ 120 µm S</td></tr>
<tr><td colspan="2">***Fig. I.1.1:*** *Results from the lithographic evaluation of POSS-based materials at IMEC under 193 nm exposure. Exposure dose: 8 mJ/cm*^{2}</td></tr>
</table>

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 µm 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.

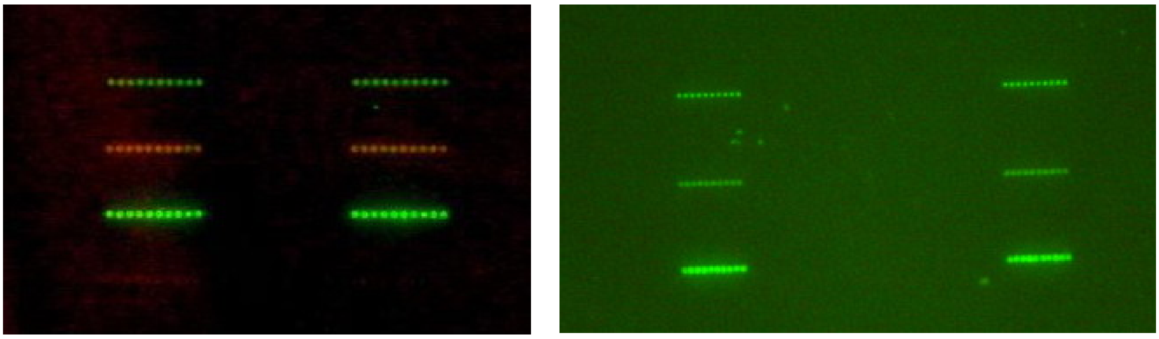


Fig. I.1.2: *Protein microarrays fabrication with our resist-based lithographic methodology.*
Left: *Rows of 1,5 μm dots. Three proteins coupled with their counterparts, which are labeled with different fluorescent markers are shown.* ***Right:*** *0.75 μm dot arrays of the same protein fabricated in 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 <10μm 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.

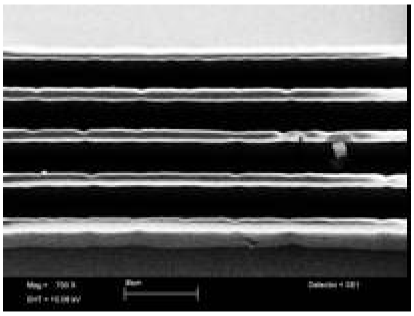


Fig. I.1.3: *Top down SEM image from resist structures with critical (lateral) dimension 5μm and aspect ratio = 6*
Resist ADEPR. Exposure 2MeV protons. Exp. dose 344 nC/mm^2

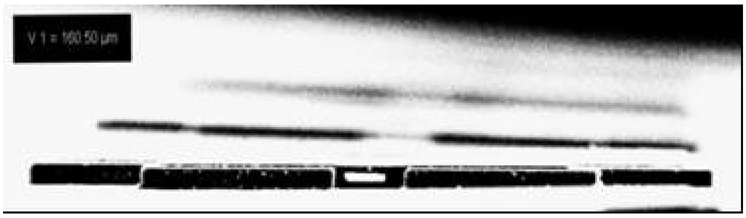


Fig. I.1.4: *Typical closed microchannel from epoxy-based resists. Length 800µm width 200µm*

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. I.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. I.1.6*).

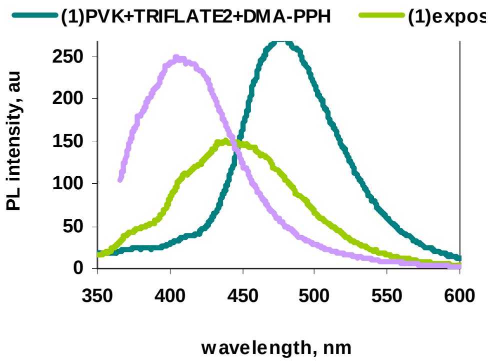


Fig. I.1.5: *Photochemically induced shift of DMA-PPH emission spectrum.*

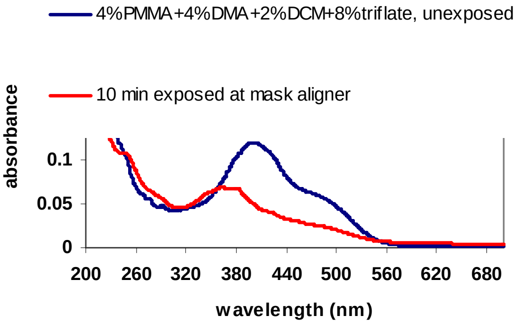


Fig. I.1.6: *Characteristic absorption spectrum changes of the two fluorescent dyes inserted in a host polymeric material before and after the irradiation.*

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

i. Measurement of Glass transition temperature

Within the research project MoreMoore (IP funded from EU) and with collaboration with Clariant the evaluation of the OPTI methodology developed at IMEL (*fig. I.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. I.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.

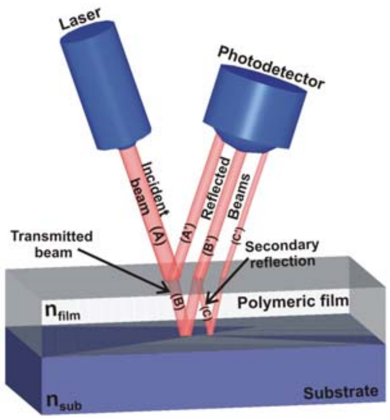


Fig. I.1.7: *OPTI (Single wavelength Optical Interferometry) principle of operation.*

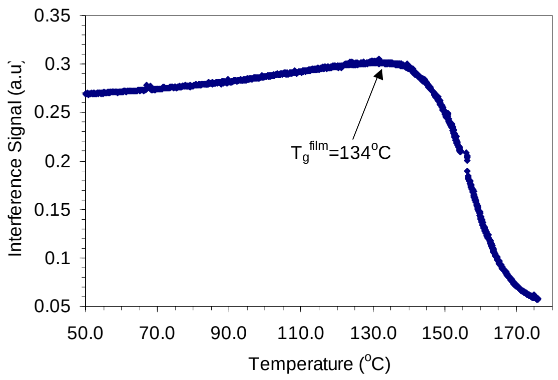


Fig. I.1.8: *Interferogram in the case of 400nm thick MMC2 film on Si substrate.*

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. I.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*)).

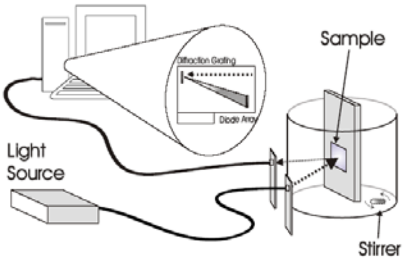


Fig. I.1.9: *Multiwavelength dissolution rate monitoring apparatus.*

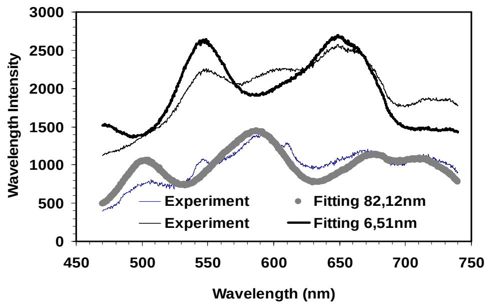


Fig. I.1.10: *Comparison between experimental and fitted, with intereference equation, spectrums at two instances.*

PUBLICATIONS in INTERNATIONAL JOURNALS

1. "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)
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)
3. "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)
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)
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)
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)
7. "Resists for nanolithography", P. Argitis, *Encyclopedia of Nanoscience and Nanotechnology, H.S. Nalwa ed., American Scientific Publishers,* (March 2004)
8. "157 nm Laser Ablation of polymeric layers for fabrication of biomolecule microarrays", Douvas, P.S. Petrou, S.E. 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

1. “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
2. “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
3. “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
4. “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)
5. “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

1. 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
2. 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