PROJECT I.1

LITHOGRAPHIC AND FUNCTIONING MOLECULAR MATERIALS

Project Leader: P. Argitis

Key Researchers: P. Argitis, I. Raptis
Other collaborating researchers: D. Davazoglou, N. Glezos, E. Gogolides, K. Misiakos, P. Normand
Post-doctoral Research Associates : M. Chatzichristidi, A. Douvas, G. Patsis, M. Vasilopoulou,
Ph.D. candidates : D. Drygiannakis, D. Niakoula, P. Pavli, N. Tsikrikas

Funding

- INTEL- MoleEUV, collaboration project for EUV resists, 2003-2006
- More Moore, EU FP6 Integrated Project (IST), 2004-2006
- Nano2Life, EU FP6 Network of Excellence (NMP), 2004-2007
- PENED "CMOS-NANO" project (GSRT-PHOTRONICS funding), 2005-2008
- Greece-Hungary bilateral cooperation (HARM.PB), 2005-2006

Research orientation

a. Development of resist platforms for next generation lithography

Development of resists with potential for sub 45 nm patterning : "molecular" resists, polymer back-bone breaking, exploration of resist resolution limits

b. Understanding and Optimization of Resist Patterning Processes : Material, Physicochemical and Process Studies

Priority in understanding the physicochemical phenomena encountered in ultra thin polymeric films and interfaces, and in molecular resists

c. Materials research for new micro-nano fabrication processes

Investigation of materials issues for novel radiation-assisted patterning processes, including formation of 3D structures, patterning of biological systems and photochemically-induced tuning of emission properties in OLEDs

d. Evaluation of new molecular classes as candidate components of lithographic or functioning microelectronic materials

Molecules which are not conventionally used in microelectronics are investigated for potential use either as components of lithographic materials or as functioning components of microelectronic devices following top-down or self-assembling processes

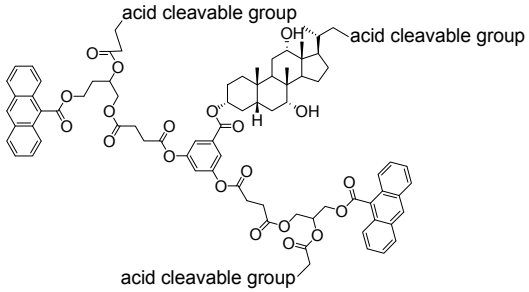
RESEARCH RESULTS

A. Development of Resists for next generation lithography

a_1 Evaluation of polycarbocycle-based molecular resist materials for sub 50nm EUV lithograhy

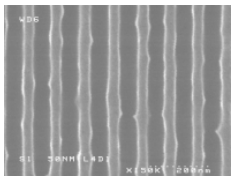
The new resist platform introduced by our group and Prof. E. Couladouros group at the Inst. of Physical Chemistry, based on the design and synthesis of new functionalized polycarbocycle molecules, was further evaluated in the context of the European project “More Moore” (2006 -) and the collaboration project with Intel.

The high resolution evaluation was mostly performed in collaboration with LETI . The EUV exposures were performed at Paul Sherrer Institute in Switzerland and e-beam exposures at LETI. Additional EUV exposures were carried out at MET (Berkeley). Close spaced sub 50 nm patterns were obtained with the resist formulation having as main component the molecule M17, after systematic process studies. The research continues towards sensitivity improvement by both material and process optimization.

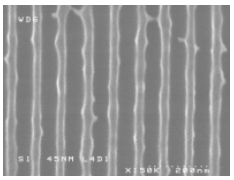


M17

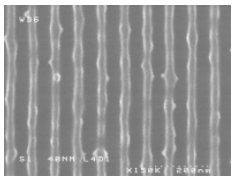
Fig. I.1.1: *Close-spaced patterning with molecular resist developed in NCSR Demokritos, which is based on the M17 polycarbocycle, using interference lithography at PSI(Harun Solak). Process optimization in collaboration with LETI (Cyril Vannuffel, Damien Djian, Serge Tedesco).*



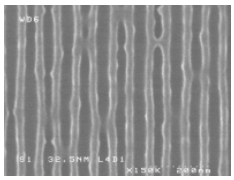
lines 50nm



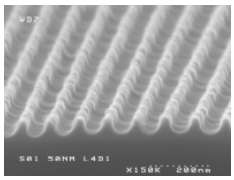
lines 45nm



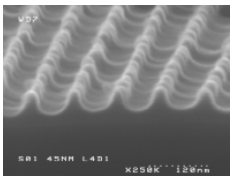
lines 40nm



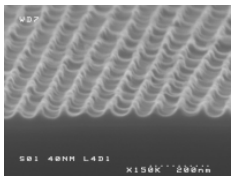
lines 32.5nm



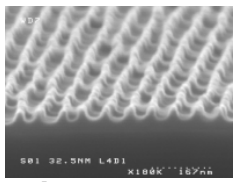
lines 50nm



lines 45nm



lines 45nm



lines 32.5nm

a_2 Resists based on backbone breaking

Backbone breaking is considered as an interesting direction for sub50 nm lithography since the Line Edge Roughness (LER) can be ultimately controlled by the size of the part of the polymer being broken and not by the polymer molecular weight. The problem is that the typical resists working by backbone breaking chemistry (e.g. PMMA) typically suffer from poor etch resistance properties since they decompose easily in the reactive plasmas used in etching. A recent direction of our research targets to overcome this problem. Promising results have been obtained so far by a polymer containing acid breakable but not photochemically active acetal bonds in the backbone.

B. Understanding and Optimization of Resist Patterning Processes: Material, Physicochemical and Process Studies

b_1 Simulation of e-beam patterning of complex layouts

For the fabrication of ICs in the sub-65nm nodes, the semiconductor manufacturing industry has the need to explore design for manufacturing (DFM) solutions that improve predictability, quality and yield. The complex mask data need to be verified and optimized before the fabrication process. An effective method to this direction would be to simulate the mask image and compare it with the design image for inconsistencies. With these problems in mind, a home made stochastic lithography simulator and an electron-beam exposure – pattern convolution module are integrated in order to result in a complete lithography simulator to account for high resolution layouts fabricated with electron-beam lithography. The application of stochastic modeling techniques is preferred in these length scales because all microscopic phenomena can be considered, through appropriate assignment of occurrence probabilities. In particular, the stochastic approach is applied in the simulation of resist film (polymer chains and PAG content), post-exposure bake (PEB) and development processing steps.

This combined stochastic - electron-beam simulator is applied in particular test layouts. Using this simulation approach both Critical Dimension (CD) and LER studies could be carried out on the same part of the layout, while the effects of processing conditions and photoresist materials on the design rules could be studied. In addition, LER quantification can be carried out in the length scale of each transistor in the layout and in a batch mode.

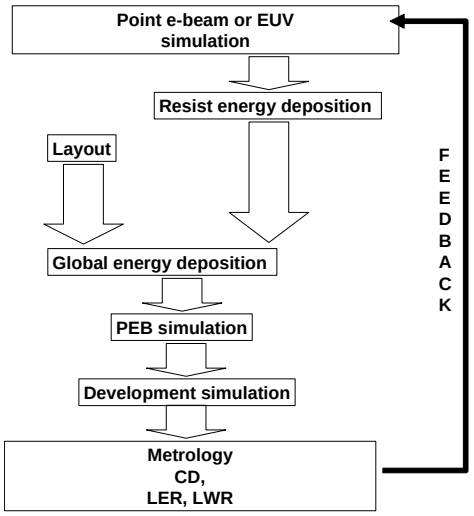


Fig. I.1.2: *Proposed simulation flowchart. Metrology on the final simulated profiles will feedback input (material/process parameters) in order to optimize the final profile prior to actual transfer of the layout on mask. LER studies can also be incorporated in this framework*

b_2 Characterization (Physicochemical properties) of thin resist films

The significantly reduced resist film thickness to be used for the 32 and 22nm technology nodes poses significant changes on the physicochemical properties and the dissolution properties compared to the thick films. The dissolution properties of molecular based resists were studied, for film thickness 80-100nm, for various formulation (PAG load) and processing (PAB temperature, PEB temperature, exposure dose) conditions. For this study a White Light Reflectance Spectroscopy methodology bas on interference was developed and applied. From these studies the resist composition (PAG concentration) and processing conditions (PAB, PEB conditions) for controlled dissolution were defined. At these conditions it was revealed, from high resolution EUV exposures, the lithographic performance was in the sub 35nm range.

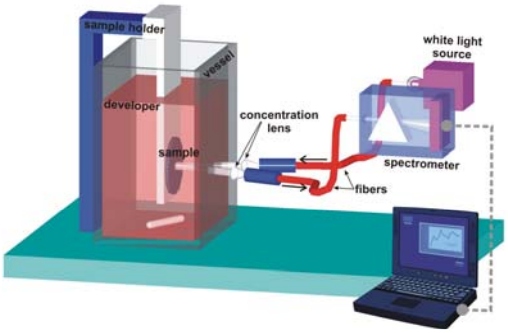


Fig. I.1.3: *Experimental set-up for evaluating dissolution properties*

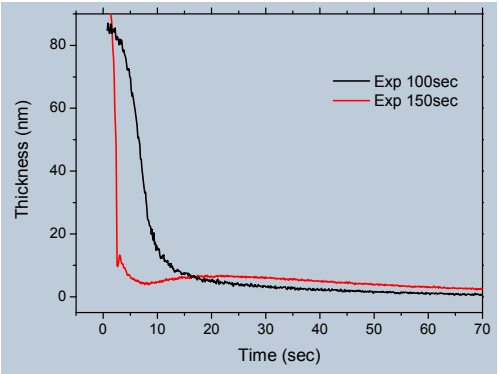


Fig. I.1.4: *Typical results demonstrating capability for monitoring dissolution processes after different exposure doses in thin (100nm or thinner) molecular resist films*

b_3 Stochastic simulation of "molecular" and oligomer-based resists

Stochastic Monte Carlo techniques are used with a quasi-static dissolution algorithm to simulate dissolution of polymer lattice based on the concept of critical ionization. Etching is simulated by applying an isotropic deformation on a numerically obtained line edge. Two-dimensional simulations and comparisons of the LER between films of molecular resists and resist films made of oligomers with the same molecular diameter showed that in all cases molecular resists have lower LER. Explanations of this behaviour were based on molecular architecture and the free volume distribution in the resist film. It was also found out through simulation, that the size of free volume regions is less in molecular resist than in the corresponding oligomers. In general, LER is minimum for low average degree of polymerization resists, low acid diffusion range (however, it should be appropriate for correct CD), and low secondary electron blur (SEB should be zero if possible to eliminated shot noise especially if combined with low ADP resists). Etching can be used to remove high frequency components of resist edges LER, but could deteriorate CD unacceptably in this trimming process.

C. Materials research for micro-nano structure fabrication

c_1 Thick film patterning technologies for the fabrication of Microsystems

Tilted structures in either thin or thick films are very interesting for various applications such as photonic crystals and microchannels. Such structures could be also used for gas/liquid handling on chips. In collaboration with the Inst. of Nuclear Research, Hungarian Academy of Sciences, a thick resist film technology based on tilted proton beam (PB) irradiation for the realization of sloped structures was developed. PB Writing is promising for the fabrication of tilted structures due to the fact that the proton beam does not broaden too much due to the interaction with matter for a large depth. In the present work, high resolution and high aspect ratio polymeric structures in SU-8 and ADEPR (aqueous developed negative resist) were resolved. The developed technology is further applied for the fabrication of long tilted microchannels clear from one end to the other with critical dimension less than 10 μm by exploiting a goniometer setup. This methodology could be applied for the implementation of "fence" structures and could be further extended to the fabrication of particular photonic structures, such as Yablonovite-type by an additional exposure to a third axis.

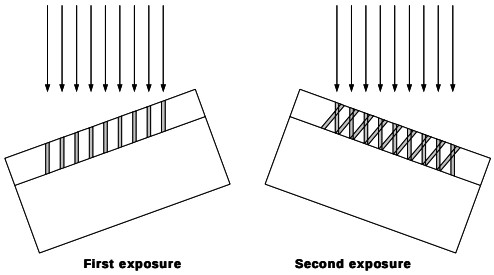


Fig. I.1.5: Schematic representation of the tilted exposures at the goniometer setup. The sample was tilted to +20° for the first irradiation, then -20° for the second irradiation, and kept a well defined alignment point in the microscope view to make sure that the two irradiations will overlap

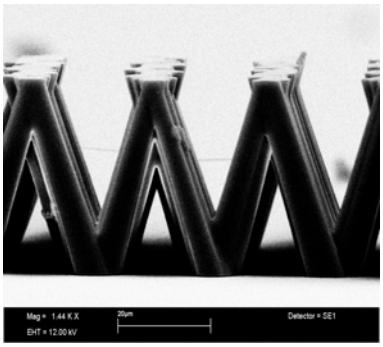


Fig. I.1.6: Side view of the "lambda" structures of SU-8. The length of the channel is 100 µm and the wall thickness is 10 µm.

c_2 Investigation of interactions between organic surfaces and biological materials

Towards the further development of resist – based biocompatible processes for the patterning of biological substances a research effort aiming at the investigations of the interactions of organic film coated substrates with biological substances has been launched. Emphasis is given on the interactions of proteins and oligonucleotides with photoresist surfaces but other organicic films, especially photochemically active polymeric films and self-assembling monolayers (SAMs) are considered.

c_3 Photoacid induced emitting colour changes in OLEDs

The research effort to further improve the proposed by our group patterning scheme of acid induced spectral changes in the active layer of OLEDs was conrinued. Three colour (blue-red-green) pixels have been defined (see figure). The influence of the patterning process on the efficiencies of the devices has started.

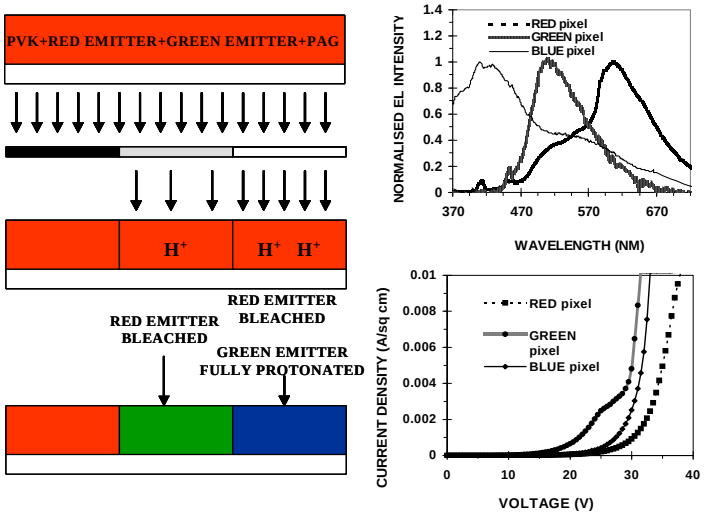


Fig. I.1.7: Proposed patterning scheme for the formation of three colour (blue-red-green) emitting pixels in a single layer in OLEDs. Characteristic electroluminescence spectra and IVs from different colour pixels are shown.

D. Evaluation of selected molecular classes as candidate components of lithographic or functioning microelectronic materials

d_1 Polyoxometallates

The class of Mo and W polyoxometallates, which can be considered as molecular analogs of the corresponding oxides is investigated for three different areas of applications :
a) Development of lithographic materials and nanostructuring processes with polyoxometallates as photosensitizers or as etch resistant components
b) Development of layer by layer processes for the fabrication of organized polyoxometallate single layers or multilayers that are evaluated as candidate components of memory devices in collaboration with researchers of program II (see relevant section of project II.2).
c) Development of electrochromic materials where certain polyoxometallates act as strong acids in solid state.

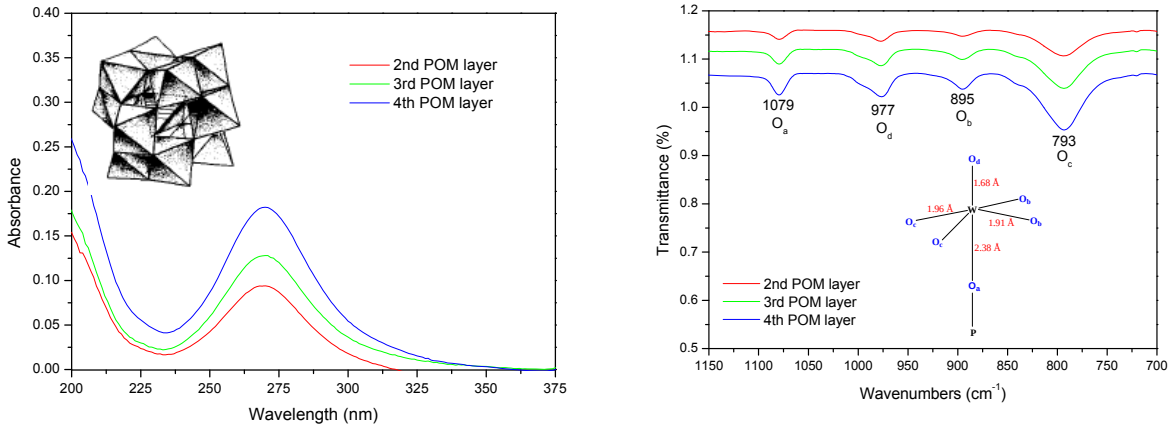


Fig. I.1.8: *UV-Vis (left) and FTIR (right) spectroscopic monitoring of layer by layer process, where the* $PW_{12}O_{40}^{3-}$ *(Keggin structure anion) is deposited using a selected diamine as the cation layer*

d_2 Functionalized polyaromatics

Polycarbocyclic molecules of the same class as the ones used as basic components of the molecular resists described above, which are based on derivatized anthracenes, are investigated as components of photonic materials with potential applications in OLEDs or in integrated sensing devices. The molecules are synthesized mainly by Dr V. Vidali and other researchers of Prof E. Couladouros' Organic Synthesis group in the Inst of Phys. Chemistry. The development of molecular glasses that are patternable and at the same time are functioning as photonic and charge transporting materials is considered as the main driving force for this research activity.

d_3 Macrocyclic rings

Ligand exchange reactions of metalloporphyrins were studied in collaboration with Prof. A.G. Coutsolelos of Dept. of Chemistry, Univ. of Crete. These reactions were investigated for potential application in chemical sensing devices. In particular the photochemical dechlorination of chlorinated solvents and the subsequent formation of photochemically inert Mo metalloporphyrins having chloride as one of their ligands was demonstrated. These reactions can be easily followed by UV-Vis spectroscopy. Possibilities for the use of metalloporphyrins or other macrocycles as functional elements of sensing or actuating devices are explored.

PROJECT OUTPUT IN 2006

Publications in International Journals

1. "Partially fluorinated, polyhedral oligomeric silsesquioxane-functionalized (meth)acrylate resists for 193 nm bilayer lithography", A.M. Douvas, F. Van Roey, M. Goethals, K.G. Papadokostaki, D. Niakoula, E. Gogolides, P. Argitis, Chemistry of Materials 18 (17), 4040-4048, 2006.
2. "Photochemically-induced ligand exchange reactions of ethoxy-oxo-molybdenum(V) tetraphenylporphyrin in chlorinated solvents", A.M. Douvas, P. Argitis, A. Maldotti and A. G. Coutsolelos, Polyhedron, 25, 3427-34, 2006.
3. "Protonic methacrylate polymeric electrolytes for all-solid-state WO_3-based electrochromic displays", M. Vasilopoulou, I. Raptis, P Argitis, G. Aspiotis and D Davazoglou, Microelectron Eng., 83, 1414-1417, 2006.
4. "Electrical characterization of molecular monolayers containing tungsten polyoxometalates", Nikos Glezos, Antonios M. Douvas, Panagiotis Argitis, Frank Saurenbach, Juergen Chrost and Christos Livitsanos, Microelectronic Engineering, 83, 1757-1760, 2006.
5. "Layer-by-layer UV micromachining methodology of epoxy resist embedded microchannels", M. Kitsara, M. Chatzichristidi, D. Niakoula, D. Goustouridis, K. Beltsios, P. Argitis and I. Raptis, Microelectronic Engineering, 83, 1298-1301, 2006.
6. "Electron beam lithography simulation for the fabrication of EUV masks", G.P.Patsis, N.Tsikrikas, I.Raptis, N.Glezos Microelectron. Eng. 83 1148(2006)
7. "Off line metrology on SEM images using gray scale morphology", E.N.Zois, I.Raptis, V. Anastassopoulos Microchim. Acta 155 323(2006)
8. "Pattern guided structure formation in polymer films of asymmetric blends", J.Raczkowska, A.Bernasik, A.Budkowski, P.Cyganik, J.Rysz, I.Raptis, P.Czuba Surf. Sci. 600 1004(2006)
9. "Multi-wavelength interferometry and competing optical methods for the thermal probing of thin polymeric films", N.Vourdas, G.Karadimos, D.Goustouridis, E.Gogolides, A.G.Boudouvis, J.-H.Tortai, K.Beltsios, I.Raptis J. Appl. Polym. Sci. 102 4764(2006)
10. "Thickness-dependent glass transition temperature of thin resist films for high resolution lithography", S.Marceau, J.-H.Tortai, J.Tillier, N.Vourdas, E.Gogolides, I.Raptis, K.Beltsios, K.van Werden, Microelectron. Eng. 83 1073(2006)
11. "Nano-scale spatial control over surface morphology of biocompatible fluoropolymers at 157 nm", E. Sarantopoulou, Z. Kollia, A. C. Cefalas, A.M. Douvas, M. Chatzichristidi, P. Argitis, S. Kobe, Materials Science and Engineering C, in press, available online 17 November 2006.
12. "A biomolecule friendly photolithographic process for fabrication of protein microarrays on polymeric films coated on silicon chips", P.S. Petrou, M. Chatzichristidi, A. M. Douvas, P. Argitis, K. Misiakos and S.E. Kakabakos, Biosensors and Bioelectronics, in press, available online 5 October 2006.

Publications in International Conference Proceedings

1. "Stochastic simulation studies for the dissolution of molecular resists", D. Drygiannakis, G. P. Patsis, I. Raptis, D. Niakoula, V. Vidali, E. Couladouros, P. Argitis, E. Gogolides, Abstract book, 32nd International Conference on Micro- and Nano- Engineering,MNE 06, September 2006, Barcelona Spain, *3rd poster award*.
2. "Photolithographic Process, Based on High Contrast Acrylate Photoresist, for Multi Protein Patterning", M. Chatzichristidi, P.S. Petrou, A. Douvas, C.D. Diakoumakos, I. Raptis, K. Misiakos, S.E. Kakabakos, P. Argitis, , Abstract book, MRS 2006 Fall Meeting, Boston, USA, November 27-December 1, 2006, p.96.
3. "Patterning Scheme Based on Photoacid Induced Spectral Changes for Single Layer, Patterned Full Colour Light Emitting Diodes", M. Vasilopoulou, A. Botsialas, G. Pistolis, P. Bayiati, P.S. Petrou, N. Stathopoulos, M. Rangoussi, P. Argitis, Abstract book, MRS 2006 Fall Meeting, Boston, USA, November 27- December 1, 2006, p.520, to appear also in online Proceedings.
4. "Dissolution studies of polycarbocycle-based aqueous base developable molecular resists", D. Niakoula, D. Drygiannakis, I. Raptis, G. P. Patsis, P. Argitis, E. Gogolides, V. P. Vidali, D.R. Gautam, E. A. Couladouros, W. Yueh, J. Roberts, R. Meagley, Abstract book, 19th International Microprocesses and Nanotechnology Conference, MNC, October 2006, Kamakura, Japan.
5. "Evaluation of molecular glass resists performance for 32 nm node resolution and beyond", D. Djian, J. Simon, C. Vannuffel, D. Niakoula, P. Argitis, E. Gogolides, I. Raptis, V. Vidali, E. Couladouros and A. Robinson, Abstract book, Sematech EUVL Symposium, October 2006, Barcelona, Spain.
6. "Proton beam micromachined channels in negative tone resist materials", I. Rajta, M. Chatzichristidi, E. Baradács, Gy. Deák, I. Raptis, E.S.Valamontes, Abstract book, 10th Int. Conf. Nuclear Microprobe Technology & Applications July 2006 Singapore, Singapore
7. "Effect of magnetic-field on metal-insulator > transitions in Bi wire structures", M. Chatzichristidi, Th. Speliotis, I. Raptis, I. Haritantis, D. Niarchos, C. Christides Abstract book, 32nd International Conference on Micro- and Nano- Engineering,MNE 06, September 2006, Barcelona Spain

8. “Exchange bias in ferromagnetic - antiferromagnetic submicron structures”, G. Manginas, M. Chatzichristidi, Th. Speliotis, D. Niarchos, Abstract book, 32nd International Conference on Micro- and Nano- Engineering,MNE 06, September 2006, Barcelona Spain
9. “Polymer self-assembly with lasers at 157 nm”, E. Sarantopoulou, Z. Kollia, A. C. Cefalas, M. Douvas, M. Chatzichristidi, P. Argitis, S. Kobe, E-MRS IUMRS ICEM 2006 Spring Meeting May 2006 Nice, France

Conference Presentations

1. M. Chatzichristidi, A. Douvas, P. Oikonomou, K. Misiakos, I. Raptis, C.D. Diakoumakos, P. Argitis, P.S. Petrou, S.E. Kakabakos, Photoresists for the fabrication of protein microarrays via multi-cycle lithography, Book of Abstracts, 6th Hellenic Conference on Polymers, Patras, 3-5.11.06, pp.118-9.
2. A. M. Douvas, K. G. Papadokostaki, K. Yannakopoulou, D. Niakoula, E. Gogolides, P. Argitis, Polyhedral-Oligomeric-Silsesquioxane (POSS) containing Resists for 193 nm Bilayer Lithography : The Effect of Partial Fluorination on the Lithographic Behaviour, Book of Abstracts, 6th Hellenic Conference on Polymers, Patras, 3-5 November 2006, p. 120

Technical Reports

Final Report on Intel funded project
“MolEUV : Novel Molecules for EUV Lithography - A new approach to photoresist design, coupled with fractal description and molecular simulation of roughness”, August 2006

PhD thesis

Dimitra Niakoula, Chemist, Thesis title: Polymeric materials and processes for lithography in thin films, Department of Chemistry, Polymer Science and Applications Graduate Program, University of Athens, Thesis Defense : November 2006

Patent Applications

1. P. Argitis, E. Gogolides, D. Niakoula, V. Vidali, E. Couladouros, R. Gautan, “Molecular resists based on polycarbocycle derivatives”, Greek Patent (OBI) appl. 20050100472/ 16-9-2005, International Patent Application PCT/GR06/000050 19/9/2006
2. P. Argitis, G. Pistolis, M. Vasilopoulou, Tuning the emitting color of single layer, patterned full color Organic Light Emitting Diodes, Greek Patent (OBI) appl. No 20060100359, 19 June 2006