PROJECT I.1 FUNCTIONAL MOLECULAR MATERIALS
FOR LITHOGRAPHY AND ORGANIC/MOLECULAR ELECTRONICS

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Research orientation

a. Optimization of lithographic materials and patterning processes - Development of new resists for high resolution, low LER lithography

Current activities include resists based on polymer back-bone breaking, resists based on unconventional imaging approaches, and experimental/simulation studies for supporting material and process optimization.

b. Lithographic materials and processes for micro-nano structure fabrication in MEMs and Nano-biotechnology

Investigation of material and process issues related to conventional and novel lithographic schemes proposed for patterning in the areas of MEMs, bio-MEMs and related fields

c. Materials research for organic/molecular electronics

Materials research and device architecture studies for molecular/organic electronics. Current activities include materials for molecular memories, organic light emitting diodes (OLEDs), photovoltaics and new optoelectronic devices.

Funding

- Nano2Life, EU FP6 Network of Excellence (NMP), 2004-2008
- GSRT-PENED 03ED276, “Critical sub-100nm Industrial scale Patterns for CMOS – NANO Architectures, (CMOS-NANO), 2005-2008
- GSRT-NON-EU 467, "Proton Beam NANOliithography for high aspect ratio structures of optical COMPONENTs" (PB.NANOCOMP), 2006-2008
MAIN RESULTS IN 2008

a. Optimization of lithographic materials and patterning processes – Development of new resists for high resolution, low LER lithography

E-beam and Proton-beam lithography simulation for the patterning of high resolution structures

Several alternative lithographic technologies have been suggested as potential candidates for the mass-production of integrated circuits in the next technology nodes (22nm and beyond) such as nanoimprint lithography, interference lithography etc. One of those technologies is the Mask-Less Electron Beam Lithography (ML-EBL). One of the very recent approaches in this area is the application of a shaped beam through Patterned Beam Defining Aperture (3rd-order imaging approach). The effect of beam edge acuity on resolution and LER of that particular approach is reported.

A 3D accurate electron beam matter interaction model is combined with a detailed material stochastic simulation for the simulation of e-beam edge. The particular EBL simulator is capable to handle multi-layer substrates, a feature very important in the case of direct writing. The energy deposited (EDF) from a point beam is calculated by a Monte Carlo module. The EDF is then convoluted with the beam used for the actual writing either with trapezoidal or Gaussian profile (Fig. 1). The resulted convoluted EDF is used as input in the stochastic simulation module, which models in detail the polymer chains in the resist film, photoacid generator (PAG) initiation, acid diffusion, and finally resist dissolution. This way it is possible to simulate the LER and correlate it with the edge acuity of the original beam profile. Fig. 2a, shows a 45nm square pattern simulated with the trapezoidal (left) and the rectangular beam (right). The initiate PAG concentration, and the resulted shape of the square after resist dissolution in the case of a resist film consisting of linear, or randomly grafted chains are also shown in Fig. 2. Measuring LER on the final resist edges results in the LER values shown in Fig. 3, while the corresponding average CDs are shown in Fig. 4. These quantitative graphs indicate that indeed increasing edge acuity decreased LER and improved nominal CD replication on the printed pattern.
The e-beam lithography simulation approach described above was applied also for the simulation of Proton Beam Writing (PBW), a promising high resolution lithographic technology. For the PBW simulation, a complete model of proton energy transfer from a proton beam to a photosist film was developed.

By applying the simulation software presented in the previous section, the PBW interaction with matter was explored. In Fig. 5 the energy deposition vs. sample’s depth, due to point PB exposure, for 18μm PMMA film thickness is illustrated. The limited energy deposition dependence of the energy deposition with the resist depth (increased by 17% only) is one of the advantages of the PBW over the EBL for the patterning of thick films. In Fig. 6 the energy deposition vs. lateral dimension for various resist depths is presented. It is clear that the beam broadening is very small regardless the very high film thicknesses and certainly is considerably smaller compared to the broadening in EBL. This limited beam broadening is the second advantage of the PBW over the EBL for thick resist film patterning. These two advantages make the PBW the ideal approach for mask-less patterning of high aspect ratio structures limited only by the initial proton beam diameter and the ability of the resist material to withstand high aspect ratio structures. In Fig. 7 the energy deposited, cross-section, for a line exposure is illustrated, while in Fig.8 the actually negligible proximity effect is proven for a layout including a cross pattern. In the EBL case, the proximity would cause significant deviations of the resulted trenchwidth over the whole line length.
Processing effects on the dissolution properties of thin chemically amplified photoresist films

Resist film thickness is anticipated to be 60 nm in the 22 nm technology node setting significant processing challenges due to resist non-bulk behavior. The changes in the dissolution rate of a commercial positive DUV polymer based chemically amplified resist platform due to various processing conditions such as film thickness, exposure dose, and thermal processing conditions, was experimentally investigated. It was quantified among others, the way an increase of PAB temperature deteriorates dissolution rate at low exposure dose, while in higher exposure doses increasing PAB temperature enhances dissolution rate. Also, an analytic model for the dissolution rate was imported on a stochastic lithography simulator and first quantitative results for thin films are reported.

Fig. 7: Energy deposition profile (cross-section) for a 40nm wide line exposed with a beam of 100nm diameter.

Fig. 8: Absence of proximity effect in PBW

Fig. 9: Film thickness evolution of 65nm thick AZ6270 films, processed at various PAB conditions, for two exposure doses (low and high)

Fig. 10: Film thickness evolution of 65nm thick AZ6270 (AZ-EM) films for a wide exposure dose range. Unexposed films are dissolved smoothly with a low Dissolution Rate (DR). At high doses, two DR are observed.
A new imaging approach based on a thermally developable, etch resistant molecular material

A new imaging approach that is allowed by molecules with certain molecular structure characteristics as the 1,8 Naphthalenedimethanol (Fig.11) was introduced by our group. This molecule is soluble and can form films by spin coating, although it is also suitable for vacuum deposition. It was found that in the presence of a photoacid generator and after exposure in the 248 nm area (exposure at 193 nm is also possible) the sublimation temperature changes dramatically as shown in Fig. 12.

The proposed mechanism and the imaging principle are also shown in Fig. 11. In acidic environment 1,8 Naphthalan is created by the cyclization of 1,8 Naphthalenedimethanol [1]. The produced 1, 8 Naphthalan has lower sublimation temperature than the 1,8 Naphthalenedimethanol so that in the PEB step only the exposed area is developed. In figure 12, IR spectra for the 1,8 Naphthalenedimethanol without and with addition of PAG are presented. We can follow the sublimation of the initial diole by the dramatic reduction of all the peaks in the IR spectrum. In the left spectrum, this reduction occurs at ~ 150 °C but after the addition of PAG and exposure, the reduction occurs at ~ 60 °C. The produced chemical compound (ether) is indeed expected to have a distinctly lower sublimation temperature than the initial diole, due to the dramatic reduction of the intermolecular bonding.

1,8 Naphthalenedimethanol-based films showed very good etch resistance performance as expected by the high aromatic content of the compound. In this respect it seems that there is improvement in comparison with other thermally devolapable systems studied in the past. It should also be noticed the close structural resemblance of the studied molecule with the currently investigated polyaromatic compounds in the field of organic electronics suggesting that this approach may find applications in patterning schemes for this area as well.

Fig. 11. Imaging Principle. The initial 1,8 Naphthalenedimethanol has distinctly higher sublimation temperature (~150 °C) compared with the produced 1,8 Naphthalan (~60 °C)

Fig 12. IR spectra for several temperatures. Left: Films without PAG, Right: Films with PAG.

b. Lithographic materials and processes for micro-nano structure fabrication in MEMs and Nano-biotechnology

Photolithographic approaches in bio-surfaces functionalization

The chemical binding of biotin derivatives on patterned epoxy resist (EPR), which was first proposed by our group last year, has been further advanced. The epoxy resist used is a high resolution material that can be applied for the fabrication of submicron structures with deep UV
exposure but has also been proved capable for sub 100 nm lithography if a suitable form of radiation, for instance e-beam, is used. The innovative aspect in this method relies in the fact that the epoxy resist is used for the creation of the microstructures and at the same time as substrate for covalent binding of biomolecules. The important factor of the proposed process is to tune the lithographic performance of the resist while keeping its chemical binding capacity in order to achieve the maximum resolution and the highest binding performance. Unmodified biotin and biotin derivatives have been tested for binding on unexposed resist and on resist exposed at different doses. The best results were obtained using the sulfo-NHS-LC-biotin. Using the lithographically sufficient dose, arrays of spots with diameter of 0.5 to 50 microns were created through covalent binding of sulfo-NHS-LC-biotin. The immobilized biotin was detected under a fluorescence microscope after reaction with AlexaFluor® 546 labeled streptavidin. As it shown in Fig. 6, spots with good morphology and intra-spot homogeneity were obtained for the whole range of spot diameters tested. The binding of biotin onto the microstructures created following the proposed method can be applied for the immobilization of any biotinylated protein onto the microstructures by exploiting the biotin streptavidin linkage. To confirm the chemical activity of the epoxy film, the fluorescence substance fluorescein was also immobilized on an epoxy patterned surface using the reactive fluorescein isothiocyanate ester (FITC). As it is shown in Fig. 13, FITC was also immobilized very effectively onto the photolithographically defined epoxy microstructures. Conclusively any substance that can react with the epoxy resist can be patterned onto the surface and thus, the proposed method can be applied for a wide range of applications beyond patterning of biomolecules. It must be noted that the size of the structures that can be created is limited only by the capacity of the exposure tool whereas at the same time photolithography offers unlimited freedom concerning the structure shape.

**Fig. 13.** Fluorescence images of (a) 50 μm biotin spots, (b) 0.5 μm biotin spots and (c) 5 μm FITC spots created to an epoxy patterned surface. The insert in (b) is a blow-up showing details of the spots.

**New photoacid generation approach based on Dawson polyoxometallates**

The capability of ammonium 18-molybdodiphosphate, (NH₄)₆P₂Mo₁₈O₆₂, and ammonium 18-tungstodiphosphate, (NH₄)₆P₂W₁₈O₆₂, to generate acid photochemically within polymeric films with hydroxyl functional groups was demonstrated by our group. The polymer mainly investigated was the poly(2-hydroxyethyl methacrylate) (PHEMA). Upon UV irradiation both 2:18 polyoxometalates (POMs) investigated are reduced with concomitant oxidation of PHEMA and generation of acid, which subsequently catalyzes the crosslinking of PHEMA. The photoacid generation was monitored with an appropriate acid indicator (4-dimethylamino-4′-nitrostilbene, DANS) using UV spectroscopy. By comparing the efficiency of both POMs to induce acid-catalyzed crosslinking of PHEMA under similar conditions, the W based ion is found to be more efficient in photoacid generation than the Mo based ion. Imaging of the POM-containing PHEMA films through UV photolithographic processing was demonstrated. It should be emphasized that both POMs can be entirely leached during the development step by using pure water as developer, resulting to patterned PHEMA films (fig.14). This characteristic renders the investigated POMs attractive materials for applications especially in the area of biomaterials where removal of the photoacid generator from the film at the end of the process is desirable.
Fabrication of [Co/Bi]n wire structures

[Co(1 nm)/Bi(2.5 nm)]n (n = 10 or 20) line structures on the Si(0 0 1)/SiNx substrate were fabricated by conventional patterning and deposition steps for the evaluation of the grain-boundary resistance’s contribution to the magneto-transport properties. The fabrication involves 2 lithographic and 2 sputtering deposition steps, leading to 5 rectangular-shaped and parallel magnetic lines with thickness 60 nm and line width 2 μm. A rectangular magnetic pad is attached to each line. First, the layout for the magnetic wires is transferred on a photoresist film spin coated on a Si(100)/SiNx (100 nm) substrate. Then, the substrate is covered with a 60 nm thick magnetic film via sputtering and a lift-off process of the photoresist follows. The wafer with the magnetic wires is covered again with the photoresist and after a second lithography step, the layout of the electrodes appears. Finally, sputter deposition of a thin Cr (20nm) buffer layer and 350nm thick Au layer is followed by a lift-off process of the photoresist, resulting in well defined line structures with pad.

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**Fig. 14.** Lithographic process based on photoacid generation by ammonium salts of Dawson polyoxometallates resulting to PHEMA imaging.

**Fig. 15.** SEM image of the fabricated device. Five [Co/Bi]n-lines are crossed by four Au electrodes.

**Fig. 16.** Higher magnification of the structures, showing details of Au-electrodes crossing one magnetic pad and one magnetic line.
c. Materials for organic/molecular electronics

Polyoxometallates as potential molecular components of electronic devices

Polyoxometallates of Mo and W are investigated as potential molecular components of electronic devices and in particular memory devices based either on electron or on proton transport and storage. The relevant activities are carried out in collaboration with Project II.3 (Project Leader N. Glezos) and Project II.2 (Project Leader P. Normand) and the results are reported in the corresponding sections.

Hybrid polymer-inorganic light-emitting diodes with solution-processed polyoxometalates as electron transport layers

Improved performance single-layer polymer light-emitting diodes (PLEDs) based on polyfluorene derivatives were demonstrated. A thin solution processed hydrophilic tungstate polyoxometalates layer, such as H$_3$PW$_{12}$O$_{40}$, was introduced between the green emitting copolymer poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(1,4-benzo-[2,1',3]-thiadiazole)] (YE) and the cathode (Fig. 17) and its role was examined in the improvement of the device performance. Improved efficiencies by a factor of up to 1.5 (Fig. 17) were achieved as a result of the improved electron injection and transport at the cathode/POM interface in PLEDs. Possible mechanisms for improved device performance in the context of energetic level alignment at the cathode/POM interface (Fig. 18) are investigated.

Fig. 17. Device structure (left) and J-V-L characteristics (right) of a YE PLED having a thin POM layer inserted between the cathode and the active layer.

Fig 18. Energy level diagram of a YE/POM LED
Hybrid polymer-inorganic solar cells with solution-processed polyoxometalates as exciton blocking/optical spacer

Improved performance bulk-heterojunction photovoltaics (PVs) based on donor/acceptor polymer (regioregular poly(hexyl-thiophene)/fullerene ([6,6]-phenylC70-butyric acid methyl ester) heterostructures upon inserting a thin layer of POM (Fig. 19) was demonstrated. It should be noticed that POMs represent a family of inorganic molecular oxides well known for their comparable with TiO2 properties in the area of photocatalysis. In the case of PVs the improved performance upon the insertion of POM (Fig 19.) is attributed to the enhanced absorption as well as the exciton blocking ability of POM in PVs (Fig. 20).

Fig 19. PV device structure with POM layer(left) and J-V characteristics (right) where increased photocurrent suggests improved absorption in the P3HT:PCBM bulk.

Fig 20. Overall increased absorption in the spectral region where the P3HT:PCBM active layer absorbs when POM is used as an optical spacer.
Tuning the emitting colour of OLEDs: Towards device performance optimization and new applications

Continuing the research activity on the emission tuning of OLEDs following a photochemical route proposed by our group two years ago (M. Vasilopoulou et al., Adv. Funct. Mater. 2007), we worked towards the optimization of devices performance and the exploration of new possible applications of this technology in the area of all plastic microsystems.

It was first shown that the addition of photoacid generations (necessary in our emission tuning approach) inside the emissive layer of OLEDs can result in improved charge injection. Fig. 21 (left). Although the luminance is in certain cases quenched, (e.g. when triphenyl sulfonium hexafluoroantimonate is used) the use of selected PAGs, such as the triphenyl sulfonium triflate, results to overall improvement of the device performance as shown in Fig. 21 (right).

On the other hand blue emitting flexible PLEDs based on either PVK or BE-120 were fabricated and an anti-rabbit IgG antibody, labeled with two different fluorescent dyes (ALEXA or PHYCO) was then adsorbed on the PET substrate. The blue light output of the PLED excited the fluorescent dye resulting in a red shift of the initial spectrum. The size of the shift depends strongly on the concentration of the fluorescent label. The quantum efficiency of the emitting polymers as well as the optimization of the PLED device characteristics play significant role to the sensitivity of this system. The ability to create patterned multi colour PLEDs onto the same substrate, which has been demonstrated by our group two years ago, can improve the selectivity upon different biomolecules present in the same sample by implementing a spectrally different fluorescent label for each biomolecule (Fig 22). The proposed solid-state PLED arrays are simple to construct, have low cost, low power consumption and are entirely flexible.

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Fig 21. Influence of the addition of photoacid generators in the emissive layer of OLEDs, using as host polymer the Poly[2-(6-cyano-6-methyl-heptyloxy)-1,4-phenylenederivative (commercial name BE 120).

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Fig 22. Schematic representation of our approach towards a photopatterned 3-colour PLED device for the simultaneous detection of biomolecules labeled with different fluorescent dyes.
PROJECT OUTPUT IN 2008

Publications in international Journals


Publications in international Conference Proceedings


Presentations in international Conferences


Awards

Young Researcher's Award for the Best Poster Presentation to the graduate student Dimitra G. Georgiadou in the 1st International Symposium on Flexible Organic Electronics (IS-FOE), Halkidiki, Greece, July 2008, for the paper :


Patent Applications