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Nanoscience Foundries and Fine Analysis

D3.2 Design of Nanolithography Facility

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Deliverable D3.2: Design of Nanolithography Facility

1. INTRODUCTION

1.1. Purpose of the document

The purpose of this document is to describe the concept for a NFFA Nano-Bio lab for synthesis and research on combined organic/inorganic nanoscale systems and its integration in a NFFA-RI.

1.2. Application Area

The targets of this document are the members of the NFFA Project, the EC Project Officers, and the general public.

1.3. References

Description of Work (DoW). See at web site: http://www.nffa.eu/UserFiles/file/Annex_1_DoW.pdf

The design study is based on information shared by NFFA partner facilities and during discussions with representatives from several other institutions in the frame of workshops: 1st NFFA Workshop (June 2009), Co-Nanomet Workshop (September 2009), SP&AC Workshop (December 2009). Valuable contributions were also collected during visits at the Molecular Foundry, Berkley and the MPI for Colloids and Interfaces, Potsdam.

1.3.1. Objective of Work Package 3

The Objective of WP3 is the design study of NFFA-RI centres, the technical layout of instrumentation and tools.

1.3.2. Description of work broken down into tasks

The following tasks are defined in WP3:

- T3.1) Design study of the overall infrastructure
- T3.2) Design study of a nanolithography station within the facility
- T3.3) Design study of user-oriented material growth facilities
- T3.4) Design study of user-oriented metrology facilities
- T3.5) Design study of a molecule and nano-particle manipulation lab
- T3.6) Design study of nano-bio labs
- T3.7) Assessment of the possible contribution of existing facilities that could be integrated in NFFA-RI

2. EXECUTIVE SUMMARY

A main driving force for fine analysis at large scale facilities (LSFs) is the fact that materials display very different properties at sub-micron or even nanometre dimensions. In this context the proposed nanolithography stations will play a key role within the facilities offered in the frame of NFFA centres, as they will enable the users to obtain nanostructured materials, nanostructured templates, and nanodevices, with precisely defined dimensions and geometries. In addition, fine analysis at LSFs can profit from advances in nanofabrication techniques, e.g. in the field of optics for x-ray microscopes. Moreover, LSFs themselves can be used to push the frontiers of nanofabrication.

At present, some equipments of this kind are operated directly by the LSF facilities or by collaborating institutions, which is generally not sufficient for the in-house needs (both in terms of quality and availability) and certainly it is not sufficient for external user operation. In this report, we first analyze the possible impact of nanolithography techniques for LSF users. From this we derive a set of relevant technical criteria in order to judge the usefulness of various nanolithography techniques, in particular in context with research applications in user mode operation. A set of the most promising techniques and pieces of infrastructure is identified, and an efficient distribution among the different NFFA centres is indicated. This set includes well established techniques such as electron-beam lithography or photolithography as well as recently emerging approaches, e.g. extreme ultraviolet (EUV) interference lithography or dip-pen lithography.

Closely related to the nanolithography are pattern transfer techniques necessary to delineate nanostructures into underlying layers, allowing for complex combinations of materials and functionalities. Even though in some cases no clear distinction to thin film growth techniques can be made, the main techniques are briefly reviewed and a required set of tools is listed within this part of the Design Study.

An analysis of capital investment and staff requirements is given at the end of this report.

3. MOTIVATION

A large fraction of research in nanoscience involves technologies to control the lateral dimensions of nanostructures in a top-down, deterministic way. The actual definition of a nanometre sized pattern in two or sometimes even three dimension is a key element in a typical fabrication chain to obtain nanostructures and nanodevices. During this lithography step, the desired pattern is often first defined in a resist layer, which is complemented by etching techniques or thin film deposition processes for pattern transfer (see also D3.3).

Optical based nanolithography techniques and the related tools have reached an enormous degree of maturity and perfection, as they have been pushed in context with the commercial fabrication of very large scale integrated circuits (VLSI) dictated by the miniaturization trend forced by Moore's law. In parallel, alternative approaches have been developed opening up additional opportunities for nanolithography in science, with affordable equipment and processing costs. As will be outlined in the following, various lithography techniques have to be made accessible to researchers involved in fine analysis at large scale facilities.

It seems obvious that there is a close link between the definition of structures by nanolithography techniques and the investigation of their properties on the nanometre scale by fine analysis at LSFs. To fully appreciate the potential of lithography, it is useful to have a more differentiated view on this synergy.



3.1 Nanopatterning of materials for fine analysis at LFSs

Fig. 1 Geometrically frustrated magnetic kagome ice structures created by electron beam lithography. (a) SEM images and (b) synchrotron PEEM images of kagome ice structures with three, two and one ring revealing the magnetization state.

Nano-materials significantly change their physical properties compared to the bulk materials. Nanolithography can provide means to control the lateral dimensions of nanostructures and arrangement with high resolution and accuracy. Prominent examples can be found in electronics engineering, physics¹, optics or nanomagnetics research². As the signal during the fine analysis of individual nanostructures is intrinsically low, nanolithography techniques can be used to provide large numbers of identical structures, often arranged in periodic arrays. This aspect will be of increasing importance with the advent of intense FEL sources, which may require a very frequent replacement of the sample under investigation due to radiation damage.

3.2 Nanofabrication of templates for nanoscale materials

When materials are under study that cannot be patterned directly, top-down nanolithography can be combined with bottom-up approaches. Nanometre sized templates have been used for the guided self-assembly e.g. of block-copolymer structures³, colloids⁴ or for the growth of semiconductor nanowires⁵ and nanodots⁶. Periodic arrays of nanofluidic channels have been applied to reveal ordering phenomena in

confined liquids by x-ray small angle scattering⁷. At future X-FEL sources, coherent diffraction imaging experiments on macromolecules at X-FEL sources can profit from templates to create ordered arrays of protein nanocrystals⁸.

3.3 Nanodevice fabrication for fine analysis at LFSs

Nanolithography can enable researchers at LSFs to perform fine analysis on systems of increasing complexity that include working nano-devices. These devices range from very simple ones such as local electrical heaters or thermocouples, to more complex structures like micro-coils for fast magnetic switching⁹ (see Fig. 2), or electrical contacts for studies on electromigration¹⁰.



Fig. 2 Microcoil for observation of ultrafast magnetic switching in synchrotron based PEEM.

3.4 Nanolithography using LSFs

An additional close link between nanolithography and a synchrotron LSF is given by the fact, that xrays are not merely used for analysis, but also for nanofabrication itself. The short wavelengths applied in xray lithography or EUV interference lithography bares the potential of high resolution, while the high brilliance is favorable in terms of throughput (see further below).

Nanolithography techniques can significantly contribute to improving the performance of fine analysis at LSFs. These applications include the fabrication of test objects with well defined nanostructures for benchmarking and calibration of x-ray microprobes or diffraction gratings for x-ray wave front analysis and the testing of x-ray mirror optics¹¹. In particular, advanced electron-beam writing techniques are applied to produce high resolution x-ray lenses. Nanofocusing refractive lenses (NFLs)¹² and Fresnel zone plates (FZPs) used as diffractive lenses can be applied in x-ray microscopy (see Fig. 3). These devices provide the highest spatial resolution values of all x-ray optics. Recently, sub-10 nm structures have been resolved for the first

Fig. 3 Refractive (left) and diffractive (right) high resolution x-ray lenses used at microscopy and nanoprobe beam lines.

time¹³, and further progress will boost the results obtained with x-ray microscopes in the fields of, biology, materials- and environmental sciences. Again, the radiation of X-FELs will pose special requirements on x-ray optics due to the high degree of coherence and extreme radiation load. Damage issues need to be addressed either by applying new materials such as diamond to x-ray optics fabrications or by developing schemes to of disposable optics that are replaced after each experiment.

4. RELEVANT TECHNICAL CRITERIA

In order to identify the optimum set of infrastructure for nanolithography in context with the proposed NFFA Centres we identify the following technical criteria to judge the relevance of the various nanolithography methods and tools.

4.1 Resolution and accuracy

The lateral dimensions that can be realized vary greatly depending on the applied lithography method. Resolution values ranging from the 1 micron range in photolithography mask aligners down to the atomic level for some scanning probe tools. In many applications, the placement accuracy in the write area or the overlay accuracy between several writing steps is also crucial.

4.2 Flexibility

The large variety of nanolithography applications require techniques, which allow for the fabrication of complex patterns on a large variety of substrates. Pattern origination methods are more flexible than techniques based on replication a master structure. In addition, it should be noted that certain techniques are limited regarding pattern geometry, e.g. to periodic structures.

4.3 Throughput

Throughput is not of the same relevance in research as it is in the commercial production of nanodevices. Moreover, the area to be patterned is usually not bigger than the beam size at a LSF (i.e. up to a few square millimetres). However, it may be necessary to produce nanostructures over areas as large as many square centimetres especially when large series of identical nanostructures are needed, i.e. for experiments in life sciences requiring disposable samples. As can be seen from Fig. 4, the throughput may varies by more than 10 orders of magnitude.

4.4 Robustness

The success rate of a process step in nanolithography will be crucial for users of NFFA lithography stations, as they need a high degree of reliability to get samples prepared in time for experiments at LSFs.

Fig. 4 Schematic comparison of nanolithography methods with respect to resolution and speed/throughput. Techniques for pattern origination show a clear dependence of throughput and resolution (diagonal shape), while the speed of replication techniques is independent on structure size (vertical shape).

4.5 Process-, substrate-, and data-standards

In order to guarantee for a high degree of reproducibility and compatibility between the lithography stations of different NFFA Centres, it is essential to establish a set of standards, especially regarding the used resist materials, resist processing, substrates, and lithography CAD data. This will enable users to transfer their results between lithography stations, to take advantage of the data repository, and to add experiences into the data repository (see D4.9).

4.6 Mode of operation and access

Nanolithography equipment often is – as many tools in nanoscience – rather complicated, sensitive, and expensive. A high level of cautiousness, training, and experience is a prerequisite to reproducibly obtain good results, in reasonable time, and without damage to the equipment. Therefore, the access for users of LSFs to nanolithography equipment should be cascaded in three main modes, depending on the degree of cost and robustness:

<u>Open access</u> to nanolithography equipment implies, that the LSF users are enabled to operate the equipment themselves. Expert staff will still be required for proper maintenance of the equipment and training of the users. In the case of non-standard, advanced tools it may be advantageous to have dedicated scientific staff doing research on the technique to keep the facility at the cutting edge of technology.

<u>Limited access</u> to nanolithography station equipment implies that only users with frequent use of the tools over a long time (e.g. PhD students or researchers permanently located at the site) are allowed to operate the equipment.

<u>Remote access</u> is the mode of operation for equipment that, due to its high degree of sensitivity and extreme risk of damage by improper use, is only operated by dedicated staff. Users can be involved in the use by providing e.g. samples and exposure data files or masks.

Generally, nanolithography equipment is operated in clean room environment. In addition to low dust particle concentrations, the sensitive processing steps also require control of temperature and humidity. High resolution and accuracy also poses special demands with respect to noise, vibration, and electromagnetic stray field levels.

Another important question is, in which cases a direct vicinity to a LSFs is required. This is obviously the case for LSF-based lithographies. For technologies used in *hand on* or *hand off* access, the vicinity to LSFs should be as close as possible, while for *remote* access, this is less important.

5. NANOLITHOGRAPHY TECHNIQUES AND EQUIPMENT FOR NFFA CENTRES

Based on the criteria defined above, the main techniques will be listed in this section. A summary including cost and recommended number of tools in the lithography stations distributed over the NFFA centres is given in Table 1. A distinction is made between techniques allowing for the origination of patterns (3.1 - 3.3) and those that reproduce patterns provided on a mask or master structure (3.4-3.5). The pattern origination methods of course provide more flexibility, which is a key point research, while replication methods are usually superior in throughput and thus advantageous if many identical nanostructured samples ore large patterned areas are required (see also Fig. 4).

5.1 Electron beam lithography

Electron-beam lithography (EBL) is a versatile technique derived from scanning electron microscopy. In brief it consists of scanning a focused beam of electrons across a surface covered with a resist film. The obtainable resolution is limited by the beam size and by the electron scattering processes in the resist material. The sequential nature of the writing makes the technique too slow for most commercial fabrication purposes. The beam deflection can be programmed in a flexible way to produce any pattern, making it a very useful, robust and wide spread technique in R&D. A high level of standardisation exists with regard to samples, resists, and exposure data. EBL should be available in all NFFA centres. Three main types can be distinguished:

SEM-based Gaussian beam EBL. A variety of vendors offer EBL solutions based on scanning electron microscopes (SEMs). The prices range from 50 k€ for simple add-on pattern generators for existing microscopes to more than 1 M€ for a complete systems based on a SEM. The results of such systems can be amazing, and for many research applications, SEM-based systems are an excellent option. They can be run in an open access, multi-user mode. There are a few fundamental limitations

Fig. 5 Schematic layout of an electron beam lithography system (taken from ¹)

regarding resolution, placement accuracy and speed, which are mainly rooted in the fact, that the original purpose of the used column was microscopy and not lithography.

<u>High-end Gaussian beam systems.</u> In contrast to SEM-based systems, all components including electron optics, sample stage, and pattern generator are designed purely for lithography purposes, and optimized for resolution, accuracy and speed. High acceleration voltages are advantageous to obtain high resolution and high aspect ratio resist structures. Therefore, the most advanced systems use 100 keV electron energy. Because of the higher degree of complexity and higher price (on the order of 2-3 M€) and running cost compared to SEM based systems, they should only be run in limited access or remote access mode. The majority of NFFA centres should be equipped with a High-end Gaussian beam EBL system.

<u>Shaped-beam systems.</u> Shaped-beam EBL systems are designed for maximum exposure speed. Instead of filling shapes by rastering them with a focused spot, the electron beam itself is shaped by variable apertures to "print" primitive shapes such as rectangles etc. This drastically increases the throughput. Such systems are mainly applied for the production of photo-masks requiring excellent placement accuracy over huge areas, but ultimate resolution is not required. Therefore, shaped beam EBL tools are not well adapted to the needs of the users of NFFA centres. Besides, the high cost of more than 5 M€ is prohibitive.

5.2 Focused ion beam (FIB) lithography

In analogy to EBL, focused ion beams can also be used for imaging and writing of nanostructures. More commonly used than the exposure of resist layers, is the direct removal of materials by FIB-milling. On the other hand, FIB can also be used to induce the local growth of materials by introducing suitable precursor gasses into the sample chamber ¹⁴, to locally implant ions and thereby change the electronic doping of semiconductor samples ¹⁵ or to define masked areas for wet and dry anisotropic etching ^{16,17}. The beam can be steered to write arbitrary patterns, and as no resists are needed, virtually any material can be machined in any geometry. So called "dual beam" FIB system have an additional SEM column that allows for in-situ positioning and observation of samples. All these possibilities give an extreme degree of flexibility to FIB lithography (see Fig.

Fig. 6 Nanostructures (text) written onto microstructures illustrating the high flexibility of FIB lithography (courtesy T. Rohbeck, FH Bremen)) 6). The resolution has reached the 10 nm level in state-of-the art systems. In contrast to resist-based techniques, FIB technology often includes already the pattern transfer.

Regarding these features it seems somewhat surprising, that lithography is not the main application of FIB technology. Instead the majority of systems is applied for inspection purposes. Here, FIB milling is used to produce cross sections of samples, e.g. for the preparation of sample transmission electron microscopy. In this context, FIB technology plays a key role in the proposed NFFA centres (see D3.4). Another common FIB application is the modification and repair of integrated circuits ¹⁸ and photomasks ¹⁹. The high potential for lithography has not been generally recognized. Only very recently, dedicated FIB systems optimized for lithography have been offered by commercial suppliers ²⁰. Such systems would be most useful in NFFA lithography stations – in addition to those used for inspection. The systems should be operated in limited or remote access mode.

5.3 Scanning probe lithography

The extremely high resolution of scanning probe microscopes down to the atomic level combined with the possibility to move the probe along arbitrary paths makes this technique very interesting for ultra high resolution lithography. However, the close proximity of the probes to the sample surface results in severe limitations regarding the obtainable speed. Typical patterned surfaces are limited to a few square microns. Moreover, the interaction between probe and surface is often quite different from other lithography techniques, and a clear distinction between lithography and manipulation (see D3.5) is not always possible. Two main types of scanning probes have shown potential in context with nanolithography.

Fig. 7 48 iron atoms arranged by STM on the surface of a copper substrate. These images show the various stages of the process (M.F. Crommie, C.P. Lutz, D.M. Eigler, Science **262** (1993) 218-220)

STM lithography. Shortly after the invention of the scanning tunnelling microscope (STM) by Binnig and Rohrer ²¹ it was realized, that also atomic scale modifications can be achieved ²², including the arrangement of single atoms ²³. As these techniques require very clean reproducible surfaces, they often need to be applied in UHV environment. A further limitation is given by the fact that only conducting surfaces allow for STM techniques. Organic self-assembled mono-24 lavers or hydrogen passivation layers on silicon ^{25,26} have been used as ultrathin resists that can be used for pattern transfer techniques.

<u>AFM lithography.</u> The atomic force microscope can provide similar resolution as an STM, but it is more flexible, robust, and fast in context with nanolithography, because the exposure mechanism, typically an electric field or current, can be applied independently of the feedback control of the tip-sampling spacing. This decoupling of the feedback control from the exposure mechanism allows the AFM to operate on insulating as well as conducting surfaces. Striking successes have been obtained, e.g. by using conduction AFM tips and local anodic oxidation, which have been used to fabricate single electron ²⁷ and quantum

electronic devices ^{28,29}. Another approach is thermomechanical writing, which allows fast patterning of polymers and other materials with extremely robustness, and 3-dimensional patterning. This approach has been exploited by IBM to developed the millipede concept, based on arrays of thousands of AFM probes for parallel patterning ³⁰.

The throughput of scanning probe lithography is still inferior to that of EBL. The strength of the method is – in addition of the resolution potential – the possibility to carry out surface modification and metrology almost simultaneously, and possibly in-situ with LSF-based fine analysis. Therefore the method should be offered to users of an NFFA centre with special emphasis on metrology. Due to the sensitivity of the analysis are used to use the sensitivity of the analysis.

the equipment, only limited or remote use is recommended.

Dip Pen Nanolithography (DPN) is a most interesting derivate of atomic force microscope based lithography. It uses the tip of an AFM to deliver molecular inks to a surface³¹, similar to Micro Contact Printing described in section 3.6. Being a constructive (bottom-up) approach to lithography, DPN has several unique capabilities. First, it can be readily carried out using parallel tip arrays ³² drastically increasing throughput combined with high resolution. Second, since no etching or post-processing is typically required, prepatterned surfaces composed of a variety of materials can be used. Finally, DPN is capable of integrating of multiple materials (or inks) with both high resolution and high throughput. This makes the technique highly interesting for biological applications (see D3.6).

Fig. 8 Fluorescently labelled phospholipids patterned on a polystyrene surface with a half-pitch of 250 nm (Courtesy Karlsruhe Nano Micro Facility).

5.4 Photolithography

Photolithography is an extremely performing process, it is the workhorse in microlithography and standard equipment in most clean-room laboratories. Transparent masks blanks with a patterned patter metal layer are copied onto a photosensitive resist layer to create structures on wafer samples. As typical exposure times are on the order of seconds, the throughput of this technique is very high, making it attractive for commercial applications. Photo lithography equipment and processes can be of very different complexity, depending on the resolution requirements.

Mask aligners position the mask in contact or in close proximity to the substrate and the absorber pattern of the mask is exposed as a direct image into the depth of the resist (1:1 shadow casting). The resolution is limited by diffraction on the mask structures to typically one micron. Because of easy handling, mask aligners are very popular in low scale production and R&D laboratories, when no ultimate resolution is required. All NFFA centres should provide open access to such equipment. Only in some cases, more

Fig. 9 Left: Mask aligner for small volume production with micron resolution. Right: Schematic view of an advanced DUV photo stepper for VLSI production with very high resolution.

specialized and sensitive tools may be operated in limited access mode to ensure optimum performance.

<u>Photo steppers.</u> Driven by the resolution requirement of very large scale integrated (VLSI) circuit production, more advanced tools have been developed that use UV radiation with wavelengths down to 193 nm. By using de-magnification optics, the requirements on the mask resolution can be reduced. Today's most advanced systems can print structures of less than 50 nm in width, at throughputs of more than 100 wafers per hour. The stunning improvement of semiconductor products according to Moore's law is particularly due to the further development in the field of photolithography ³³. However, for research

Fig. 10 Refractive lens for hard x-rays fabricated by the LIGA process using two tilted exposure steps (J. Mohr, V. Nazmov, Forschungszentrum Karlsruhe). purposes in the framework of the NFFA, the high throughput of such systems is not required, and similar or even better resolution can be obtained by other techniques such as EBL. Moreover, the very high investment (many million \in) and running cost of photo steppers cannot be justified.

<u>X-ray lithography</u>. This technique was originally developed to overcome the diffraction limits in the resolution of optical lithography for VLSI production by applying a shorter wave length ($\lambda \cong 1$ nm), typically from a synchrotron. However, it has never been commercially applied for this purpose due to various technical difficulties and the consistent improvements in optical lithography.

Interesting in context with the proposed NFFA centres is deep X-ray lithography, that uses yet shorter wavelengths ($\lambda \cong 0.1$ nm) to fabricate deeper structures,

sometimes three dimensional, with reduced resolution. The mask consists of an X-ray absorber, typically of gold, on a membrane that is transparent to X-rays. The pattern on the mask is written by electron beam lithography. The method is very useful in context with the fabrication of very high aspect ratio structures with excellent side wall quality. In combination with electroplating, the technique is called LIGA process, it is used, e.g. for micromechanical applications.

As pointed out in Section 1, deep X-ray lithography fully exploits the synergies of LSFs and micro/nanotechnology. One exposure station should be foreseen in a NFFA centre specialized on micro-and nanofabrication technologies. Limited or remote use is recommended.

UV Extreme interference lithography (EUVIL), also called x-ray interference lithography (XIL) uses diffraction masks grating with coherent 13,4 nm synchrotron radiation periodic to print nanostructures 34. Line and dot structures, but also more patterns complicated such as Fresnel zone plates can be printed fast and with very high resolution. As shown in Fig. 11, periods as small as 25 nm have been achieved, representing the world record of photon based lithography. Further advantages are the capability to print on insulating substrates and the high depth of focus. The

Fig. 11 Schematic view of extreme UV interference lithography and SEM image of 25 nm period resist structures produced by EUVIL.

diffractive masks are written by EBL, however the periods printed by EUVIL are two times smaller than the mask structures.

Even though the restriction to periodic and quasi-periodic patterns reduces the flexibility of the method, there are a large number of applications where EUVIL has proven to be most useful ³⁵. One EUVIL exposure station should be installed in a NFFA centre specialized on nanofabrication technologies, operation in limited or remote use is recommended.

5.5 Polymer replication techniques

Because of the throughput and resolution bottlenecks of known high-end lithographies, alternatives were developed that require – as long as a suitable mold can be provided – much simpler equipment. They can be used for the generation of 2D and 3D surface structures in polymers. Depending on the thickness of the material to be patterned, different variants of molding techniques exist, such as nanoimprint lithography, or high throughput methods such as roll embossing and injection molding. These replication techniques are based on mechanical contact between a master and a moldable material. In contrast to the mask in photolithography, the resolution is – because of the mechanical nature of replication – only limited by the ability to fabricate the appropriate mold or stamp. Once this tool is fabricated, it can be used for parallel patterning of large areas and retrieved after each replication step without damage. This tool needs to be fabricated by more expensive origination methods, i.e. serial techniques such as EBL. The unique advantage of molding instead of exposure is that complex stamp profiles, such as staircases, V-grooves, pyramids, both convex and concave, can be replicated in one step, and a range of moldable materials is available with appropriate mechanical and chemical properties. Although first maskshops were founded ^{36,37}, because of its higher complexity, in the near future replication techniques will only be effective if stamps and molds with the desired profile and specifications can be made in-house.

Nano-imprint lithography(NIL). In NIL only a thin layer of material on top of a rigid substrate is molded, which serves as a resist in subsequent pattern transfer processes ³⁸, ³⁹. In most cases this pattern transfer is therefore similar to high resolution (photolithography, but with higher resolutions and the ability to pattern functional resists (e.g. loaded with nanoparticles). NIL is suitable for reliable small scale production in laboratories where EBL is not available or does not provide enough area and throughput. It is also suitable for copying of expensive originals and for enlargement of surface area. Fig. 12 Shows an example where NIL has been used for the fabrication of nanopore membranes ⁴⁰. Furthermore it can also be upscaled for production, as it is currently done for patterned media and high brightness LEDs. NIL needs a cleanroom environment since it is sensitive to contamination by dust. It should therefore be installed in the majority NFFA centres which need a range of nanofabrication technologies for different

Fig. 12 Nanopore membrane chip device (a) for research on individual membrane molecular complexes with (b) structured membrane area with nanopore arrays with (c) diameter/pitch 330/600 nm, fabricated by NIL in combination with photolithography and micromachining.

applications. Specific process equipment, e.g. step&repeat machines for surface enlargement by step-wise imprint of a small stamp should be installed in limited mode.

<u>Thermal injection molding (TIM) and roll embossing</u>. TIM uses the technology base of NIL in a highly industrialized environment. Is used to generate micro and nanoreliefs on polymer surfaces of devices by filling a cavity with a polymer melt with high throughput and reproducibility. Most TIM machines are standard machines with a complex and costly mold tool. Because in contrast to NIL mold specifications are crucial, the cost involved are often prohibitive if only low throughput is needed. This is also the case for roll to roll embossing R2R), where a foil is imprinted with a nanopatterned roll in a continuous process. Both processes are scale-ups to the more versatile and less crucial hot stamper embossing (similar to NIL) and only required if high throughput is needed. Standard TIM and R2R do not need a specific cleanroom environment but profit from laminar flow to reduce contamination by dust. A few NFFA centres with a large customer base in industry should be equipped TIM machines, operated in limited or remote use is recommended.

5.6 Other replication techniques

There exist a number of further replication technologies that can be most useful for users of LSF facilities, but that require only fairly simple equipment. Only one group will be discussed here as representative:

<u>Soft</u> lithography. This group of techniques includes the technologies of Micro Contact Printing (µCP), replica molding (REM), microtransfer molding (µTM). One of the soft lithography procedures, µCP, uses the relief patterns on a Polydimethylsiloxane (PDMS) stamp to form patterns of self-assembled monolayers (SAMs) of inks on the surface of a substrate through conformal contact. The technique was pioneered by Whitesides at al. in the nineties ⁴¹. As in other replication techniques the master structure has to be originated by EBL or photolithography. Due to mechanical limitations, their resolution is lower than NIL with hard stamps. However, the softness of the stamp makes the technique less sensitive to dust particles, allowing for operation in standard lab environment. The specific advantage of µCP lies in the compatibility with biotechnology, e.g, to use the method to print precise patterns of axon guidance molecules, which are used as substrate to control the growth of axons ⁴². In this context the method should be offered to users of an NFFA centre with special emphasis on nanobiology (see D3.6). The simplicity and robustness of the technique allows for open access use.

Fig. 13 B16 cell growing on a vitronectin pattern at the border between a uniform and a patterned substrate of 1 μ m² dots fabricated by μ CP.

6. PATTERN TRANSFER TECHNIQUES

Not all, but many of the lithography techniques above can only pattern resist layers and therefore require a pattern transfer process to delineate the exposed and developed resist structures into a functional layer. This can, in principle, be achieved either by *removing* material that is not protected by the resist structures, or *adding* material. The first class is summarized in this design study as etching techniques, which can either be applied using liquid etchants or in gas phase. The second class, namely pattern transfer by deposition, includes very common techniques such as lift-off, selective deposition, or implantation of dopants.

Similar to the development of lithography techniques, the main driving force for the development of pattern transfer processes has been and still is the commercial production of integrated circuits for computing and telecommunication applications. Pattern transfer into semiconducting materials and metallic interconnects is therefore particularly well developed. Even though these classes of materials are still of relevance in context with fine analysis at LSFs, the scope of materials, and therefore also the spectrum of interesting pattern transfer processes for NFFA centres is wider.

The technical criteria relevant in context with pattern transfer processes are somewhat different than those for the pattern defining lithography processes. Since pattern transfer is generally carried out in parallel for all structures on a substrate, *throughput* is not a critical issue. Instead, criteria as *selectivity*, i.e. the effectiveness of a resist as protective layer, as well as the *anisotropy*, i.e. the capability of producing structures with high aspect ratios, is of high relevance.

6.1 Etching techniques

<u>Wet chemical etching</u>. The oldest and simplest technique for pattern transfer is the chemical removal of a substrate or substrate layer, usually in aqueous acid or alkaline solutions. A wide variety of technically relevant materials can be patterned. In most cases the etching attack is uniform in all directions, meaning that the side wall profile of the resulting structures is *isotropic*. The obtainable aspect ratios are therefore

very limited. Only in some cases the etching can be anisotropic, especially for single crystalline materials. The most prominent example is the anisotropic etching of silicon in potassium hydroxide solution, where the etching speed drastically depends on the crystal direction. An example is given in Fig. 14.

The *resolution* of etching processes can in principle be high, however in some cases the etching of polycrystalline materials will reveal grain boundaries leading to high line edge roughness. Moreover, isotropic etching will lead to line broadening. In spite of the limitations mentioned above, wet chemical etching is an indispensable and comparatively low-cost technique, which should be available in all NFFA centres. The required tools are part of any standard clean room.

Fig. 14 Examples of high aspect ratio silicon microstructures produced by anisotropic wet etching. The structure period is 4 μm.

As an alternative to liquid phase etching, a number of so-called dry etching techniques have emerged over the past decades. Here a plasma discharge is used to generate ions or chemically active radicals to attack the unprotected parts of the substrate surface. Depending on the etching mechanism and the plasma discharge generation, a whole zoo of equipment has been developed. Only the main classes of plasma etchers are described below.

<u>Sputtering etching</u> is simply based on the physical removal of substrate material upon impact of energetic ions. Usually inert Ar^+ ions are used with energies in the keV range. The high *flexibility* lies in the fact, that virtually all materials can be etched, as the method does not rely on a chemical reaction. However, the *selectivity* of resist structures is generally low, and the side walls of the etched structures are sloped, resulting in limited aspect ratios.

Reactive Ion Etching (RIE). This group of equipment applies chemically reactive plasmas e.g. from oxygen or halogen containing gasses. If the etched substrate forms a volatile compound with the plasma products, it will be removed into the gas phase. The gas composition, gas pressure, ion energy, plasma density, and substrate temperature, can be used to optimize the etching process. These techniques are very well developed, especially for silicon, silicon oxide, and polymers. Selectivity and Anisotropy can be very high, and structures with aspect ratios exceeding 20 can be produced in some cases. In addition, some metals such as Al, Ti, W, or Ta as well as compound semiconductors can be structured. In so called cluster tools, the etching process can be combined with Plasma Enhanced Chemical Vapour Deposition (PECVD, see also Fig. 15 and D3.3).

Fig. 15 Combined RIE and PECVD cluster tool (courtesy Oxford Instruments Inc.)

<u>Deep Reactive Ion Etching (DRIE</u>). Among the many types of reactive plasma etchers, DRIE using the so called Bosch process ⁴³, plays a key role in microfabrication in silicon. It is also known as pulsed or timemultiplexed etching, alternates repeatedly between two modes to achieve nearly vertical structures: a standard, nearly isotropic plasma etch that uses sulphur hexafluoride [SF6], followed by deposition of a

chemically inert passivation layer by, for instance, C_4F_8 source gas. These etch/deposit steps are repeated many times over resulting in a large number of very small isotropic etch steps taking place only at the bottom of the etched pits.

The method results in very high etch rates (several microns/minute) and it can provide extreme *anisotropy* and *selectivity*. Aspect ratios exceeding 100 have been obtained. The main commercial applications are the etching of capacitor trenches in DRAM memory circuits, and microelectromechanical systems (MEMS), see Fig. 16. For research in context with NFFA centres, a variety of very interesting applications can be envisioned, ranging from x-ray optics to microfluidic devices. Therefore several DRIE machines must be available.

Fig. 16 MEMS comb drive produced by DRIE

6.2 Pattern transfer by deposition

Instead of etching, a resist pattern is often transferred by *Lift-off technique*, which is based on the coating by physical vapour deposition of the patterned resist layer and the selective removal of the resist coated parts in a solvent.

Fig. 17 SET device made by e-beam lithography and sloped liff-off technique (courtesy T. Weimann, PTB Braunschweig)

The method is very popular due to its high *flexibility* as a wide variety of materials can be deposited. *Selectivity* and *anisotropy* are low, limiting the obtainable aspect ratios. The processing step can often be done using the equipment listed in the thin film growth section (see D3.3). However in some applications, additional features are required, e.g. the possibility to tilt the sample (see Fig. 17). Therefore, a small number of deposition tools are listed in the table on page 19, in addition to the ones listed in D3.3.

<u>Electroplating</u> can be used for pattern transfer into some metals, mainly Au and Ni. In the LIGA technique, high aspect ratio resist structures are filled (see for example Fig. 10) by electro-deposition. This method has been successfully been transferred to nanometre sized

structures. Alternatively, a complete negative replica can be produced, which can then be used as master structure for polymer replication (see section 5.5). This technique is of huge commercial interest e.g. for the production of CDs and DVDs, and highly interesting research applications in context NFFA can be envisioned, e.g. the fabrication of disposable polymer nanodevices for nano-biology research.

The required tools reach from very simple and cheap DC deposition baths to highly advanced pulse plating machines. The latter are only required in NFFA centres with a special bias on nanolithography.

<u>Implantation</u> of doping atoms can also be considered as a deposition technique to transfer a resist pattern into a substrate. This technique is of utmost relevance for CMOS electronic device fabrication. However, the technique and the required tools for NFFA centres are covered in D3.3 on material growth facilities.

7. COST ESTIMATE

In the tables below, the various lithography tools and pattern transfer techniques for NFFA centres are listed summarizing the criteria defined in section 4. In the lower part of the table, the required number of tools and manpower, both scientific and technical staff, is given. The numbers are based on the assumption, that four NFFA centres are created.

Lithography techniques												
	Pattern origination lithography						Mask based / replication lithography					
	Electron beam lithography			Focused	Scanning	Photo lithography				Replication		
	SEM	High-end	Shaped	lon Beam	probe	Mask	Photo	EUV-IL	X-ray	NIL	Injection	Other
	based	Gaussian	beam	lithography	lithography	aligner	stepper		lithography		moulding	replication
Resolution	high	very high	medium	high	ultimate	low	high	Very high	high	Very high	high	medium
Flexibility	high	high	medium	Very high	medium	high	medium	Very low	low	medium	medium	Medium
Throughput	medium	high	Very high	low	Very low	Very high		high		high	Very high	High
Robustness	high	high	high	high	low	high	high	medium	high	high	Very high	High
Level of	medium	high	high	low	Very low	Very high	Very high	low	low	medium	medium	Low
standardization												
Access mode	open	Limited/	remote	Limited/	limited/	open	remote	Limited/	remote	open	remote	Open
		remote		remote	remote			remote				
Required	Lab or	Clean-room	Clean-room	Lab or clean-	Lab or in-situ	Clean-room	Clean-room	in-situ at LSF	in-situ at LSF	Clean room	Lab or clean-	Lab
environment	clean-			room	at LSF						room	
	room											
		-	-	-1	-2		-			-		-
Required units	3	3	0	2-	2-	6	0	1	1	3	1	4
Cost per unit	0,8	3,0	>5	1	0,4	0,4	10-20	0,5	1,0	0,5	0,5	0,05
(M€)												
Total investment	2,4	9,0	0	2.0	0,8	2,4	0	1,0	1,0	1,5	0,5	0,2
(M€)												
Dedicated staff	1	2	2	1.5	1	0,5	2	2	2	1	1	0,5
per unit												
Total staff	3	6	0	3	2	3	0	2	2	3	3	2

Table 1

¹ In addition to FIB systems for inspection purposes (see D3-4) ² In addition to SPM systems for inspection/metrology purposes (see D3-4)

Pattern transfer techniques									
		Et	Pattern transfer by deposition						
	Wet etcl	ning		Dry etching					
	Isotropic Chemical	Anisotropic	Sputter etching	Reactive ion	DRIE	Lift-off by PVD	Electroplating	Implantation	
	wet etching	Si etching		etching					
Resolution	Very high	Very high	high	Very high	medium	Very high	high		
Flexibility	high	low	very high	medium	low	very high	low		
(materials choice)									
Anisotropy	low	very high	medium	high	very high	low	high		
(aspect ratio)									
Selectivity	high	high	low	high	very high	very high	very high		
(of mask)									
Robustness	high	high	high	high	medium	high	medium		
Level of	high	high	high	medium	high	medium	medium		
standardization									
Access mode	open	limited	limited/remote	limited/remote	remote	limited/remote	limited/remote		
Required	Lab or clean-room	clean-room	Lab or clean-	Clean-room	clean-room	Lab or clean-	Lab or clean-		
environment			room			room	room		
Required units	8	3	3	8	3	4 ³	2	04	
Cost per unit	0,05	0,1	0,3	0,3	0,8	0,4	0,2	1	
(M€)									
Total investment	0,4	0,3	0,9	2,4	2,4	1,6	0,4	0	
(M€)									
Dedicated staff	0,2	0,5	0,5	0,5	1	0,3	0,3	0	
per unit									
Total staff	1,6	1,5	1,5	4	3	1,3	0,6	0	

Table 2

³ In addition to PVD systems listed in D3.3 ⁴ In addition to implanters listed in D3.3

8. REFERENCES

- ¹ Adrian Bachtold, Peter Hadley, Takeshi Nakanishi, Cees Dekker. *Logic Circuits with Carbon nanotubes* Science **294** (2001) 1317
- ² J.I. Martin, J. Nogues, K. Liu, J.L. Vicent, I.K. Schuller *Ordered magnetic nanostructures: fabrication and properties* Journal of Magnetism and Magnetic Materials **256** (2003) 449
- ³ S.O. Kim, H.H. Solak, M.P. Stoykovich, N.J. Ferrier, J.J. de Pablo, and P.F. Nealey, *Epitaxial self-assembly of block copolymers on lithographically defined nanopatterned substrates*, Nature **424** (2003) 411
- ⁴ F. Juillerat, H.H. Solak, P. Bowen, H. Hofmann Fabrication of large-area ordered arrays of nanoparticles on patterned substrates
 Nanotechnology 16 (2005) 1311
- ⁵ L.E. Jensen, M.T. Bjork, S. Jeppesen, A.I. Persson, B.J. Ohlsson, L. Samuelson Role of surface diffusion in chemical beam epitaxy of InAs nanowires Nano Letters **4** (2004) 1961
- ⁶ D. Grützmacher, T. Fromherz, C.Dais, J. Stangl, E. Müller, Y. Ekinci, H.H. Solak, H. Sigg, R.T. Lechner, E. Wintersberger, S. Birner, V. Holy and G. Bauer, *Three-dimensional Si/Ge quantum dot crystals*, Nano Lett. **7**(10), 3150-3156 (2007)
- ⁷ A. Diaz, C. David, H. Guo, H. Keymeulen, F. Pfeiffer, G. Wegdam, T. Weitkamp, J.F. van der Veen *Microcavity arrays for X-ray diffraction studies of ordering phenomena in confined colloid solutions* Physica B **357** (2005) 199
- ⁸ C.M. Kewish, P. Thibault, O. Bunk, and F. Pfeiffer *Potential for two-dimensional crystallography of membrane proteins at future X-ray free electron laser sources* submitted to: Nature Photonics (2009)
- ⁹ H. Stoll, A. Puzic, B. van Waeyenberge, P. Fischer, J. Raabe, M. Buess, T. Haug, R. Höllinger, C. Back, D. Weiss, G. Denbeaux, *High-resolution imaging of fast magnetization dynamics in magnetic nanostructures* Appl. Phys. Lett. 84, (2004) 3328
- ¹⁰ H.H. Solak, C. David, J. Gobrecht, M. Drakopoulos *Imaging X-ray Topography Technique for the Analysis of Electromigration Induced Stress* Journal of Physics D: Applied Physics **36** (2003) A128
- ¹¹ T. Weitkamp, B. Nöhammer, A. Diaz, C. David, E. Ziegler *X-ray wavefront analysis and optics characterization with a grating interferometer* Applied Physics Letters **86** (2005) 054101
- ¹² C. G. Schroer, O. Kurapova, J. Patommel, P. Boye, J. Feldkamp, B. Lengeler, M. Burghammer, C. Riekel, L. Vincze, A. van der Hart, M. Küchler, *Hard x-ray nanoprobe based on refractive x-ray lenses* Appl. Phys. Lett. **87** (2005) 124103
- ¹³ J. Vila-Comamala, K. Jefimovs, T. Pilvi, J. Raabe, R.H. Fink, M. Senoner, A. Maaßdorf, M. Ritala, and C. David Advanced Thin Film Technology for Ultrahigh Resolution X-Ray Microscopy Ultramicroscopy **109** (2009) 1360-1364
- ¹⁴ G. M. Shedd, H. Lezec, A. D. Dubner, J. Melngailis *Focused ion-beam induced deposition of gold* Appl. Phys. Lett. 49 (1986) 1584-1586
- ¹⁵ M. Li, J. Wang, L. Zhuang, S.Y. Chou Focused ion beam gallium implantation into silicon. Appl. Phys.A. 39 (1986) 183
- ¹⁶ N. Cherukov, K. Grigoras, A. Peltonen, S. Franssila, I. Tottonen *The fabrication of silicon nanostructures by local gallium implantation and cryogenic deep reactive ion etching* Nanotechnology **20**, (2009) 065307

- ¹⁷ E. Platzgummer, H. Löschner, G. Gross Fabrication of complementary metal-oxide-semiconductor integrated nanomechanical devices by ion beam patterning Photomask Technology 6730 (2007) 73033
- ¹⁸ S. Matsui and Y. Ochiai *Focused ion beam applications to solid state devices* Nanotechnology **7** no. 3 (1996) 247–258
- ¹⁹ J. C. Morgan *Focused ion beam mask repair* Solid State Technology **41** (1998) 61
- ²⁰ J. Gierak, E. Bourhis, G. Faini, G. Patriarche, A. Madouri, R. Jede, L. Bruchhaus, S. Bauerdick, B. Schiedt, A.L. Biance, L. Auvray *Exploration of the ultimate patterning potential achievable with focused ion beams* Ultramicroscopy **109** (2009) 457
- ²¹ G. Binnig, H. Rohrer, Ch. Gerber, E. Weibel *Surface Studies by Scanning Tunneling Microscopy* Physical Review Letters **49** (1982) 57
- ²² R.S. Becker, J.A. Golovchenko, B.S. Schwarzentrüber Atomic-Scale Surface Modifications Using a Tunneling Microscope Nature **325** (1987) 419
- ²³ M.F. Crommie, C.P. Lutz, D.M. Eigler Confinement of electrons to quantum corrals on a metal surface. Science 262 (1993) 218
- ²⁴ E. Delamarche, A.C.F. Hoole, B. Michel, S. Wilkes, M. Despont, M.E. Welland, H. Biebuyck *Making gold nanostructures using self-assembled monolayers and a scanning tunneling microscope* Journal of Physical Chemistry B **101** (1997) 9263
- ²⁵ E. S. Snow, P. M. Campbell, and P. J. McMarr Fabrication of silicon nanostructures with a scanning tunneling microscope Appl. Phys. Lett. 63 (1993) 749
- ²⁶ J. A. Dagata. *Scanned Probe Oxidation* Science **270** (1995) 1625
- ²⁷ K. Matsumoto, M. Ishii, K. Segawa, Y. Oka, B. J. Vartanian and J. S. Harris Room temperature operation of a single electron transistor made by the scanning tunneling microscope nanooxidation process for the TiOx/Ti system Appl. Phys. Lett. 68,(1996) 34
- ²⁸ E. S. Snow and P. M. Campbell Fabrication of Si nanostructures with an atomic force microscope Applied Physics Letters 64 (1994) 1932
- ²⁹ R. Held, T. Heinzel, P. Studerus, K. Ensslin, M. Holland *Semiconductor quantum point contact fabricated by lithography with an atomic force microscope* Appl. Phys. Lett. **71** (1997) 2689
- ³⁰ P. Vettiger, M. Despont, U. Drechsler, U. Durig, W. Haberle, M. I. Lutwyche, H. E. Rothuizen, R. Stutz, R. Widmer, K. Binnig *The "Millipede"—More than thousand tips for future AFM storage* IBM Journal of Research and Development **44**, (2000) 323
- ³¹ R. D. Piner, J. Zhu, F. Xu, S. H. Hong, C. A. Mirkin *"Dip-pen" nanolithography* Science **283** (1999) 661-663
- ³² L. Demers, G. della Cioppa Nanotechnology to advance discovery R&D Tutorial: Dip pen nanolithography as a next-generation, massively parallel nanoarray platform Genetic Engineering News 23 (2003) 36
- ³³ T.A. Brunner, Why optical lithography will live forever, J. Vac. Sci. Technol. B 21(6) (2003) 2632-2637
- ³⁴ H. H. Solak, *Nanolithography with coherent extreme ultraviolet light*, Journal of Applied Physics D:
 39 (2006) R171.
- ³⁵ V. Auzelyte, C. Dais, P. Farquet, D. Grützmacher, L. Heyderman, F. Luo, S. Olliges, C. Padeste, P. Sahoo, T. Thomson, A. Turchanin, C. David, H. H. Solak, *Extreme Ultraviolet Interference Lithography at the Paul Scherrer Institute* Journal of Micro- and Nanolithography 8 (2009) 021204 10

³⁶ www.nilt.com

³⁷ www.eulitha.com

- ³⁸ H. Schift and A. Kristensen, Nanoimprint lithography. Chapter (Part A/8) in "Handbook of nanotechnology", Ed. B. Bhushan, second edition, rev. and extended, 2007, Springer Verlag, Berlin, Germany, Hardcover. ISBN: 978-3-540-29855-7, November 2006, XLIV, 1916 pp., 1593 illus, with CD-ROM, 239-278 (2007).
- ³⁹ L.J. Guo, Recent progress in nanoimprint technology and its applications, J. Phys. D: Appl. Phys. **37** (11)(2004) R123-R141.
- ⁴⁰ L.J. Heyderman, B. Ketterer, D. Bächle, F. Glaus, B. Haas, H. Schift, K. Vogelsang, J. Gobrecht, L. Tiefenauer, O. Dubochet, P. Surbled, and T. Hessler, *High volume fabrication of customised nanopore membrane chips*, Microelectronic Eng. **67-68**, 208-213 (2003).
- ⁴¹ A. Kumar, G. M. Whitesides Features of gold having micrometer to centimeter dimensions can be formed through a combination of stamping with an elastomeric stamp and an alkanethiol ``ink'' followed by chemical etching Applied Physics Letters **63** (1993) 2002
- ⁴² A.C. von Philipsborn, S. Lang, A. Bernard, J. Loeschinger, C. David, D. Lehnert, M. Bastmeyer, F. Bonhoeffer *Microcontact printing of axon guidance molecules for generation of graded patterns* Nature Protocols **1**, no 3 (2006) 1322
- ⁴³ F. Lärmer, A. Schilp: Verfahren zum anisotropen Ätzen von Silicium . Patent DE4241045, Germany,
 5. Dec. 1992