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Proton-Fountain Electric-Field-Assisted Nanolithography (PEN): Fabrication of Polymer Nanostructures that Respond to Chemical and Electrical Stimuli. An Overview in the Context of the Top-Down and Bottom-Up Approaches to Nanotechnology

Andres H. La Rosa  
*Portland State University*, andres@pdx.edu

Mingdi Yan  
*University of Massachusetts - Lowell*

Rodolfo Fernandez  
*Portland State University*

Elia Zegarra  
*Portland State University*

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Proton-fountain Electric-field-assisted Nanolithography (PEN):
Fabrication of polymer nanostructures that respond to chemical and electrical stimuli.
An overview in the context of the top-down and bottom-up approaches to nanotechnology

Andres La Rosa¹, Mingdi Yan², Rodolfo Fernandez¹, Xiaohua Wang¹ and Elia Zegarra¹,³

¹Portland State University, Portland, Oregon 97207, USA
²University of Massachusetts Lowell, Lowell, MA 01854, USA
³Universidad Nacional de Ingeniería, Facultad de Ciencias, Lima-PERU

I. ABSTRACT

The development of chemically functionalized materials, such that their physical properties can vary in response to external mechanical, chemical, or optical stimuli, offers potential applications in a wide range of fields, namely microfluidics, electronic memory devices, sensors and actuators. In particular, patterned structures built with stimuli-responsive polymer materials are attractive due to their inherent lower cost production and for building soft scaffolds that mimic closer natural bio-environments. In addition, harnessing the construction of patterns with nanoscale dimensions would not only a) allow building lab-on-a-chip devices that require minimal chemical reactants volumes, but also b) find applications in the area of nano-electronics for fabricating flexible, low-cost, and low-voltage-operation integrated logic circuits devices. To address these potential applications of stimuli-responsive polymer nanomaterials in the bio and nano-electronics arena, this article provides first a brief review of radiation and non-radiation based lithography methods used for fabricating nanopatterns. This introduction helps to put in context a more general description of the Proton-fountain Electric-field-assisted Nanolithography (PEN) technique, a recently introduced scanning-based method able to fabricate patterns of nanoscale dimensions using responsive polymer films. We also outline potential avenues for the outgrowth of PEN by replacing its current top-down fabrication approach with a bottom-up modality. The proposed outgrowth is to improve the fabrication speed and the lateral dimensions of the patterns. More specifically, we address the fact that, since PEN capitalizes on the reversible swelling-response of poly(4-vinylpyridine) (P4VP) films upon spatially-localized injection of protons (hydronium ions H₃O⁺), the diffusion of the positive charges inside the polymer film matrix limits the patterns lateral resolution. This shortcoming can be remediated by the integration of ultra-fast optical activation into the PEN technique in order to gain much finer control over the functionalized sample area where the polymer molecules are selectively attached to the substrate, which would allow implementing a diffusion free, nanometer resolution, self-assembly method for fabricating erasable polymer nanostructures.
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I. The development of PEN in the context of the emerging fields of biomimetic and nano-electronics

There exists a long standing interest in the biomimetic field for unraveling the inner working principles of biological systems for, ideally, building devices that closely mimic their functioning. Lipid bilayers membranes that separate cells from their external environments constitute specific example of the sophisticated mechanisms observed in biological machineries, where embedded membrane-proteins facilitate the communication between the interior and exterior sides carrying out a multitude of tasks, namely signal transduction, transportation of small molecules, catalytic reactions, etc. (See Ref. 1 provides an interesting review of intriguing mechanisms by which these molecular machines operate.)\(^1\) Interesting enough, this fascinating concerted bio-chemical work is revealed at different dimension scales. Indeed, nature provides with vast examples of highly organized hierarchical structures whose dimensions range from the micron-size (cell) to the nano-sized scale.\(^2\) An example of the latter constitutes the flagella of bacteria, which rotates at over 10,000 r.p.m. driven by a protons-flow caused by electrochemical potential differences across the membrane; the diameter of the bearing is approximately 30 nm, with an estimated clearance of approximately 1 nm.\(^3\)

On the other hand, there are increasing evidences that living cells are not just chemical factories (as tacitly implicit in the lines above) but they can also be conceived as mechanical devices,\(^4,5\) for it is found that cell membranes are very sensitive to the mechanical properties of its surrounding matrix (affecting their growth, differentiation, migration, and, eventually, apoptosis.)\(^6,7\) Incidentally, a recent report indicates that stem cells do not regenerate efficiently in vitro environment unless the surrounding medium is made out of soft materials.\(^8,9\) This new mechanical sensitivity characteristic has fueled further the development of synthetic polymer scaffold for regenerative medicine.\(^10,11,12,13\) In addition, there exists special interest for micron- and nano-sized structures. Their advantage can be contrasted within the field of tissue engineering where, for example, hydrogel scaffolds\(^14\) are found to cause premature death of cells (necrosis) due to diffusion limitations, even though these artificial scaffolds closely mimic the chemical and mechanical properties of natural extracellular matrix.\(^15\) What happens is that in large hydrogels it is difficult to control the three-dimensional architecture and cell-cell interactions, which makes it difficult to replicate the complexity of real tissues. Micron-sized hydrogels, in contrast, have no such limitations. For example, by using hydrogels of controlled sizes and shapes\(^16\), it is possible to minimize diffusion limitations while fabricating tissues with complex microarchitecture.\(^17\)

Inspired by the well-coordinated chemical and mechanical processes displayed by living cell membranes, there has been successful attempts in the design of a variety of building blocks (gels,\(^18,19\) brushes,\(^20\) hybrid systems with inorganic particles\(^21\)) that respond selectively to different (pH,\(^22\) temperature,\(^23,24\) optical,\(^15,25\) and magnetic\(^26\)) external stimuli. One particular approach within the biomimetic-materials field constitutes the development of versatile stimuli responsive thin films\(^27\) The rationale behind these efforts conceives building complex synthetic hierarchies (needed to eventually mimic nature) as a combination of functional-domains separated by stimuli-responsive polymer thin films, the latter regulating the interactions between the domain compartments.\(^28\) This vision constitutes one of the motivations for developing Proton-fountain Electric-field-assisted Nanolithography (PEN), which aims at
harnessing the fabrication of nanoscale patterning of responsive polymer films, and whose description is the subject of this article.

PEN was introduced very recently by demonstrating its ability to pattern features (of nanometer-size in height and micron-size wide) in poly(4-vinylpyridine) P4VP films. The initial selection of this polymer responded to the fact that its swelling properties, triggered by wet exposure to acids, had been previously demonstrated in experiments performed at macroscopic scales. PEN has extended this principle to the nanoscale domain, aiming to fabricate artificial scaffolds that closely mimic the mechanical properties of natural extracellular. In addition, being a polymer of conjugated type (it contains pyridine groups, with molecular orbitals, along its chain) P4VP is also being used to explore opto-electronics applications, which is timely in the current trend of research interest for developing low-cost, low-voltage operation, flexible nano-electronic devices. Altogether, the potential applications in the biological and electronics fields have triggered further the interest of our research groups for developing PEN. The first PEN demonstrations were implemented using a scanning probe modality, as described in more detail in the following sections. In this article we also explore new experimental approaches to overcome the inherent slow process associated to its scanning probe implementation and how to improve the capability to fabricate patterns with finer line widths.

This article is organized as follows. Section II provides a brief view on past and current trends in the fabrication of nanomaterials, including specific examples of the top-down approach (briefly describing radiation and non-radiation-based lithographic techniques for building single electron memory devices) and the bottom-up approach (describing the construction of self-assembly complex architectures using P4VP material.) The purpose of section II is to first provide a quick view of the underlying efforts for harnessing the fabrication of materials with nanoscale dimensions. Section III offers a summary of early results obtained using PEN, including technical details of the fabrication process with an emphasis on attaining an understanding of the working principle of the molecular “glue” used in the fabrication process; the latter is used to covalently attach polymer molecules to a substrate. Section IV outlines the integration of ultra-fast optical activation into the PEN technique in order to gain control over the specific area that will be chemically functionalized and where the polymer molecules will be selectively attached to the substrate. Such a technical outgrowth would allow implementing a diffusion free self-assembly method for fabricating erasable polymer nanostructures.

II. General trends in the fabrication of nanomaterials

Nanomaterials fabrication methods can be classified according to whether their assembly followed either i) the so called bottom-up approach, where smaller components of atomic or molecular dimensions self-assemble together, according to a natural physical principle or an externally applied driving force, to give rise to larger and more organized systems; or ii) the top-down approach, a process that starts from a large piece and subsequently uses finer and finer tools for creating correspondingly smaller structures. These two approaches are schematically presented in Fig. 1. There are advantages and disadvantages in both approaches, which are estimated according to their speed, reproducibility, and cost.
Fig. 1  a) Schematic representation of the formation of nanostructures via the top-down and bottom-up approaches.  

b) A tapered probe, manipulated by a macroscopic machine, allows “writing” small features by scratching the probe apex on a soft polymer surface. Notice the removed material disperses on the sides of the created grooves.  
*Image attained at Portland State University, Portland, Oregon, USA; courtesy of Rodolfo Fernandez.*  
c) Example of self-assembling set to occur on previously chemically-functionalized surfaces; chemisorption happens due to interactions between adsorbing molecules and specific sites on the substrate. The resulting nano-electronics material emerges with much more effective functions when proper shapes and microstructures are provided.  
*Image courtesy of Dr. Hiroyuki Sugimura, Nanoscopic Surface Architecture Laboratory, Department of Materials Science and Engineering Kyoto University, Japan.*
II.1 The “top-down” approach to nanotechnology

II.1A Photolithography silicon technology: Radiation-based method for fabricating electronic devices

One of the best examples of the top-down fabrication procedure is photolithography silicon technology,\(^3\), \(^39\) which was originally developed for microelectronics (integrated circuits planar technology) but now it is also used to make miniature machines (three dimensional structures obtained by exploiting the preferential material-etching along the silicon’s crystallographic planes.)\(^40\),\(^41\) This revolutionary fabrication process started with the invention of the point-contact transistor in 1947\(^42\) that heralded the dawn of microelectronics. Since then, the industry has been driven by the demand to build devices that squeeze an ever increasing number of individual circuit elements onto ever smaller pieces of semiconductor materials.\(^43\)

The ability to shrink the size of the devices depends on the particular lithographic technique used to make the circuit pattern. In the photolithography process outlined in figure 2, pre-designed patterns are transferred from a mask (made, for example, using electron beam lithography) to the target silicon substrate. The process comprises the following typical steps:

i) Spin-coating a thin layer of light-sensitive polymer resist on a silicon wafer sample (Fig. 2b).

ii) Subsequently the sample is illuminated with ultra-violet light through the patterned-apertures of a mask (Fig. 2c); hence only some regions of the resist are exposed to the uv-light, which causes changes in the resists’ solubility. There exist two modalities for using the mask. In the contact mode, illustrated in Fig. 2 c-1, the mask is placed in almost near-contact with the sample; this modality is prone to cause damage to both, unless very much care is placed in the procedure. This type of setting is widely used in research labs. But for applications involving large volume production, where the integrity of the components becomes an issue, the mask is instead placed at a working-distance from the sample. In this projection mode the mask features are projected through an optical system, as shown in Fig. 2 c-2, which offers a safer alternative than the contact mode. Notice however that, due to light diffraction effects, the resist’s areas exposed to radiation will be larger than the corresponding opening areas of the mask (i.e. there is a loss in resolution). This imposes limitations on lithography-based procedures for creating devices of dimensions smaller than the wavelength. Thus the semiconductor industry has also been driven to use radiation of smaller wavelength.

iii) The procedure continues dipping the sample in a developer in order to remove the resist from the places where it has been exposed to light (Fig. 2d).

iv) The resist pattern on the wafer is subsequently used to either etch material from the naked regions where the resist exposes the wafer to the etching agent (Fig. 2e) or, alternatively, to deposit additional material as required by the circuit design. Afterwards, the resist is stripped completely off the wafer (Fig. 2f).

Notice that after these four steps, features on the mask (step c) will have been transferred to the Si-substrate (step-f). This whole process is repeated as many times as required by the circuit design complexity.
Fig. 2 a) to f) Schematic diagram of a photolithography process. The asterisks on step-c1 and step-f are to highlight the fact that features on the mask are replicated onto the Si-substrate (except for some limitations imposed by light diffraction, which makes the features on the silicon to be larger than the ones in the mask.) g) Non-volatile memory cell with a (80 nm wide and 160 nanometers long) “floating gate” central storage data, built at Bell Lab using optical lithography. *Image of the non-volatile memory reprinted with permission of Alcatel-Lucent USA Inc.*

A representative example of a top of the line device manufactured using a lithography process is the non-volatile memory device shown in Fig. 2g, which stores data even when its power supply is turned off. This device is basically a metal-oxide-semiconductor field effect transistor (MOSFET), except for having a modified gate electrode. For completeness, a schematic of both is shown in Fig. 3. The top and right sides displays the working principle of a MOSFET, where a key role is played by the electron conductive channel (separated from the p-type substrate by a depletion region) that forms upon the application of a sufficiently high gate voltage (greater than a threshold voltage \( V_T \)); subsequent modification of the channel (in response to different values of the drain voltage \( V_D \)) renders transistor operation with very high input impedance and unequal low-power consumption device. The ability to modulate the conductance of the channel through a gate electrode that is isolated from the channel by a thin oxide constitutes one of its main advantages. Fig. 3 also shows a modified MOSFET where a poly-silicon floating gate is fabricated in between the control gate and the channel, separated by a thin oxide. When a positive voltage is applied to the control gate, charge is injected from...
the channel region and through the gate oxide into the floating gate. When the applied voltage is removed, the injected charge can be stored in the floating gate for a long time (days). To remove the charge, a negative gate-voltage $V_G$ is applied.

**Fig. 3 Top and right sides:** A p-type metal-oxide-semiconductor field effect transistor and output I-V characteristics. A conductive channel (or inversion layer) is formed between the source and drain $n^+$ regions when the applied gate voltage exceeds a threshold voltage $V_T$ (the latter is characteristic of the particular MOSFET device). The current $I$ vs drain voltage $V_D$ response is illustrated for a fixed $V_G$ voltage. As $V_D$ changes, the corresponding modifications of the channel controls the operation of the transistor. **Left bottom side:** Floating gate non-volatile memory. This is basically a MOSFET that has a modified gate electrode that comprises a floating gate surrounded by insulator $SiO_2$. When a positive voltage is applied to the control gate, charge is injected from the channel region through the gate oxide into the floating gate. When the applied voltage is removed, the injected charge can remain stored in the floating gate.
The finest resolution that can be achieved by optical lithography is hampered by diffraction effects (step c-2 in Fig. 2). As a rule of thumb, the smallest feature that can be fabricated using traditional optical methods is of the order of $\lambda/\text{NA}$, where $\lambda$ is the wavelength of the light being used ($\lambda \sim 500 \text{ nm}$ for visible light, 200 nm for uv) and $\text{NA} = n \sin \theta$ is the numerical aperture of the final objective lens used to deliver the radiation on the substrate ($n$ is the index of refraction of the medium separating the lens and the sample). Still, the 80 nm features in the memory device shown in fig. 2g was achieved using radiation of 193 nm wavelength. However, this was possible only due to special procedures that employed a phase-shift lithography method, together with special chemically-amplified photoresist materials. This example reveals then that, by 1999, the semiconductor industry was already struggling to continue the trend of shrinking the size of electronic devices.

The above mentioned limitations imposed by optical diffraction triggered the development of alternative strategies, including *immersion optics* (using a fluid to fill the gap between the projection-lens and the wafer surface in order to increase the numerical aperture); *absorbance modulation optical lithography* AMOL (where two different wavelengths, applied simultaneously, control the opacity and transparency of selected regions on the sample); *electron beam lithography* EBL (computer-controlled SEM with means for blanking the “pencil” electron-beam and “writing” the pattern on the sample one pixel at a time, or using more sophisticated procedures to speed up such a process including hybrid EBL-lithography approaches); *ion beam lithography* (to capitalize on the reduced lateral scattering of ions, compared to electrons, within the resist film); *soft x-ray or extreme uv-lithography* (currently the favorite 13-nm wavelength technology to replace optical lithography). All these different options are well documented in Ref. 35. For completeness, let’s mention that progress following the “top-down” route also includes the fabrication of stimuli responsive polymer brushes, growth of polymers from previously patterned templates, and chain polymerization of monomolecular layer by local stimulation using a sharp tip. The use of a tip to delineate high resolution patterns will be addressed in the section below that describes Proton-fountain Electric-field-assisted Nanolithography (PEN).

### II.1B Nano imprint lithography: Non-radiation based method to construct single-electron memory devices operating at room temperature

A quite different alternative route to overcome the lateral resolution limitations imposed by diffraction is to use no radiation at all. In this new approach, patterns on the resist are delineated no by chemical reactions triggered by incident radiation but by mechanical means instead. That is the case of *nano imprint lithography* NIL (where the resists is physically deformed using a patterned mold) and *nanostamping* (where, as its name indicates, the specific features are defined by stamping “ink” to a substrate via a pre-fabricated stamp.) To gain some grasp on how does this approach work, let’s describe the NIL with a bit more detail. Fig 4a shows schematically the NIL imprinting process, implicitly illustrating some of its virtues, namely no diffraction limited constrains (spatial resolution limited only by the ability to fabricate a proper high resolution master mold), elimination of radiation sources and optical alignment settings (which would lead to lower fabrication cost), and, very important, a viable alternative for industrial production (many devices constructed at once). In this process, first a
compression molding (coated with a thin anti sticking layer) is used to create a shallow thickness contrast pattern on a thin resists film. Afterwards, the mold is removed, and a very directional reactive ion etching process\textsuperscript{62} takes place to transfer the initially shallow pattern deeply through the entire resist thickness.

The high resolution capability of the NIL constitutes a viable alternative to large scale fabrication of electronic devices with nanometer-sized features. In particular, for example, floating gate non-volatile memory devices described in the previous section (Fig. 3), where data information is represented by storing charges on the floating gate. Such regular MOSFET devices typically use thousands of electrons to define a binary “1” state. The motivation for shrinking the size of these devices is the added benefit of faster operation speed and lower power consumption.\textsuperscript{63} What would be the ultimate limit in scaling down a floating gate memory? A provocative answer would be to use just one electron to represent a bit.\textsuperscript{64} Working in this direction, early devices of relatively large dimension (~100 nm) required cryogenic temperatures to work with such sensitivity. However, the potential of single-electron devices for integrated circuit applications at room temperature was identified as early as in 1988.\textsuperscript{65} A reduction in the size of the device to ~10 nm, so that the quantized energy level spacing becomes larger than the thermal noise, lead to an increase in the maximum operating temperature of single-electron devices to room temperature in 1995.\textsuperscript{66} The progress has not occurred, however, without difficulties. At this scale, the normally random distribution of the individual dopant atoms within the semiconductor becomes a critical factor in determining device performance. Particularly, the dopants influence the device-to-device fluctuations in the threshold voltage ($V_T$ in Fig. 3) that turns-on the device. It has been found that an orderly distribution of the dopant results in less fluctuations.\textsuperscript{67} In short, for single electron operation, a small floating gate is needed to significantly increase both the electron quantum energy levels (the narrower the gate, the more spaced the quantized energy levels) and the electron charging energy (due to the small capacitance).

Design, fabrication, and characterization of room-temperature Si single-electron memories using nanoimprint lithography NIL was reported in 2003.\textsuperscript{68} Although other approaches had succeeded using grown Si “dots” or isolated nanocrystal Si as storage dots,\textsuperscript{69} the multi-dot nature and their random location lead to a large fluctuation of the device performance, and, hence, not amenable for large-scale integration. In contrast, in the NIL approach the floating dot is formed and self-aligned with the narrowest part of the channel (see Fig. 4b) thus giving the stored electron maximum screening ability. It is found that in these devices the threshold voltage shifts with the presence of additional charges in the floating gate. Also, due to the Coulomb blockade effect,\textsuperscript{70,71} the voltage increments needed to keep charging the gate becomes discrete (and well separated). The ultimate limit in scaling down the floating gate memory is to use one electron to represent one bit.

The NIL fabrication of a single-electron memory device, outlined in Fig. 4, comprises the following steps:\textsuperscript{68}

i) The starting material is a silicon-on-insulator substrate composed of a single crystal silicon layer (35 nm thick) built on an amorphous SiO$_2$ oxide. The silicon layer is for (housing) the channel.
ii) The single crystal silicon layer is subjected to a 2.4-nm-thick oxide thermally growth in diluted O₂. This oxide is to separate the channel from the floating gate to be built on top; that is, it will constitute the tunneling region for electrons to be injected from the channel to the floating gate. Attaining a good quality oxide at this stage appears to be a key step to ensure a long retention time (more than 2 days) memory device. (Previous attempts using much thinner oxides ended up with a device having just five seconds retention time memory.)

iii) A 13 nm poly-silicon is deposited by low-pressure chemical vapor deposition, which serves as the basis material to build the floating gate.

iv) The Si layer, the oxide, and the poly-silicon layer are patterned using NIL (as outlined in Fig 4a). The double-neck tapered planar geometry of the pattern (see Figs 4b and 4c) constitutes a clever geometric design that leads, upon oxidation in the next step, to the formation of a small poly-silicon “dot.”
v) A 13.6 nm oxide is thermally grown at 850 °C in dry O₂. During the oxidation of the (Si, SiO₂, poly-Si) patterned layered, the oxide grows faster in the thin poly-Si layer, and, thus, it is completely consumed except for the formation of a small dot. This occurs due to the fact that oxidation is a self-limited process. Notice, this way the floating dot ends up self-aligned with the narrowest part of the channel. The poly-silicon dot serves as the floating memory gate.

vi) Plasma enhanced chemical vapor deposition of a 33-nm SiO₂ layer, in order to electrically isolate the silicon dot. The samples are then annealed at 850 °C in N₂ to improve the SiO₂ quality.

vii) Next, a poly-silicon layer is deposited, and the control gate is patterned to a length of 3 µm, which covers the floating gate and part of the narrow channel.

viii) After source and drain implantation, and final contact connection established, the fabrication of a memory device is achieved.

II.2 Bottom-up approach to nanotechnology

There exists a variety of examples that exploit a bottom-up route to fabricate nanostructures. Here we focused in one involving poly(4-vinylpyridine) P4VP, the same material used in the first demonstrations of PEN. This way we expose a different facet of this interesting material.

II.2A Self-organized P4VP polymer architectures

Self-organizing structural order over several length scales are possible due to several molecular interactions, including hydrophobic and hydrophilic effects, hydrogen bonding, Coulomb and van der Waals forces. In the case of proteins, for instance, multiple interactions create minima in the local free energy of the molecules as a function of different chain configurations; without these interactions, entropy causes the molecules to adopt irregular shapes with little organization. However, the calculation and measurement of energy and entropy at the molecular level are nontrivial tasks, which expose the need for developing guidelines for successfully fabricating structures at different scales. Basic principles of the spontaneous organization of simple synthetic polymers have been addressed, both theoretically and experimentally. Self-organization typically renders just the local structures (i.e., the initial step of a self-organizing process). To fully exploit the opportunities offered by the symmetry of self-organized structures, and obtain materials with directional properties at different scales, additional mechanisms and interactions (hydrogen bonding and hydrophobic interaction that promote phase separation, electric fields, topographically patterned surfaces, tailored substrate chemistry) have to be used. One particular example is presented next.

Fig. 5a shows a general bottom-up strategy for building ordered polymer structures, which combines recognition (whereby two molecules with molecularly matching complementary interactions and shapes recognize each other, thus initially forming a receptor-substrate supramolecule) with self-organization (forming long range structural order via additional interactions). The process starts with a flexible polymer that has bonding sites along its backbone (in general some precautions need to be taken to avoid coiling). The centers are then “recognized” by, and connect to, side groups (for example molecules with polar-heads and nonpolar-tails as shown in Fig. 5a) via complementary bonds (hydrogen bond, ionic...
interactions,\textsuperscript{83} etc.) thus forming comb-shaped supramolecules. Subsequently, such macromolecules self-organize.

As a specific example, Fig 5b shows that poly(4-vinylpyridine) P4VP works well under this strategy (see also Fig 6b):

\textit{i) The pyridine rings, distributed along the P4VP polymer chains, act as recognition centers.\textsuperscript{76} Optionally, acid molecules (methane sulfonic acid MSA in Fig. 6b) can be used to protonate these rings, which helps to stretch out the P4VP (due to the mutual electrostatic repulsion among the centers) and strengthen their role as receptor centers.\textsuperscript{82}}
Block copolymers (comprising of two or more homopolymer subunits linked by covalent bonds) allow building more complex architectures following similar procedure as the one outlined in Figure 5 above. Adapted from [O. Ikkala and G. Brinke, Science 295, 2407 (2002)]; reprinted with permission from AAAS. Left: Diblock copolymers (consisting of P4VP-MSA-PDP molecular complex) allow microstructural control on two length scales. Right: SEM micrograph of the complex diblock architecture. Setting the system at 150°C causes disorder in the P4VP-MSA-PDP domains, leading to the formation of hexagonal cylindrical structures (within the rest of the polyurethane and part of PDP materials). From [J. Ruokolainen et al, Science 280, 557; 1998]; reprinted with permission from AAAS.

The fabrication process continues by adding amphiphilic surfactants (molecules with polar-heads and less-polar tails, such as pentadecylphenol PDP), which form hydrogen bonds with the polymer, (see also Fig. 5b).
This procedure leads to the formation of structures with mesomorphic order of periodicity $L \approx 5 \text{nm}$ (Fig. 6b.) The layered structures result from microphase separation between the “non-polar surfactant PDP tail layer” and the “polar polymer layer” to which the surfactants are attached. (Microphase separation is similar to that of oil and water; being immiscible they phase separate.)

More complex architectures can be obtained using block copolymers (polymers derived from two or more monomeric species, as opposed to a homopolymer composed by only one type of monomer. See Fig. 6a). Block copolymers are interesting because they can "microphase separate." That is, the different monomeric components have different solubility\(^{74}\) and, therefore, they tend to separate out. But, because the blocks are covalently bonded to each other, they cannot get apart macroscopically; instead they self-organize into lamellar fashion (like grill-sheets stacked one over another), thus adding another periodicity to the architecture as the ratio of the polymer length can be arbitrarily selected. As an example, Fig. 6b shows structures whose starting materials are polystyrene(PS)-block-P4VP, with the P4VP chains forming the minority blocks.\(^{82}\) Notice the two different periodicities $L_c = 48 \text{ Å}$ and $L_b = 350 \text{ Å}$.

Additional architectures can be obtained by varying the temperature. Fig. 6c illustrates the case in which one of these ordered structures can be purposely destroyed, hence giving rise to hexagonal-cylinder porous.

**III. Top-down Proton-fountain Electric-field-assisted Nanolithography (PEN):**

Fabrication of erasable polymer nanostructures via chemical and electrical stimuli

The examples in the previous section described the use of poly(4-vinylpyridine) P4VP to build extended and complex architectures. This section focuses on complementary efforts, using Electric-field-assisted Nanolithography (PEN), for harnessing the patterning of raw P4VP films in a very localized fashion, delineating polymeric features of micron- and nano-scale dimensions. PEN could become a useful tool in the materials science and molecular engineering fields for constructing devices that rely on the transduction of environmental signals.\(^{84}\) This Section III describes the scanning-based, top-down approach, implementation of PEN in some detail. Its potential outgrowth, incorporating bottom-up approach procedures, aiming at increasing fabrication speed and pattern resolution, is outlined in Section IV.

**III.1 PEN working principle**

PEN mirrors the dip-pen nanolithography (DPN) technique\(^{85,86}\) where patterns are created by anchoring molecules onto a surface of proper chemical affinity. But, contrasting such “pilling molecule over molecule” approach, PEN was set to instead trigger the formation of nanostructures as a result of the substrate’s swelling in response to an external chemical and electrical stimuli delivered through a sharp scanning probe.\(^{29,87}\) The procedure is illustrated schematically in Fig. 7. The experimental results suggest that the pattern formation on a 50 nm thick polymer film is triggered by the local injection of protons (hydronium ions $\text{H}_3\text{O}^+$ from an acid-coated sharp solid stylus) into the substrate. The transfer of charge from the stylus into the polymer matrix film occurs provided that both the ambient humidity is above 60%\(^{88}\) and the stylus is pressed against the film with a sufficient strong force, greater than 1 $\mu \text{N}$.\(^{29}\) The high humidity facilitate the formation of a water meniscus around the tip-sample contact, which
works as a bridge assisting in the transportation of the hydronium ions from the tip to the substrate’s surface. The high force aids the ions to penetrate and subsequently diffuse into the substrate.

The presence of swollen structures just in the regions where the probe made contact with the surface suggests that the protons, upon diffusing into the polymer matrix, protonate the P4VP pyridine centers. Although the polymer matrix is electrically neutral, the electrostatic repulsion among the pyridine centers produces a net swelling effect on the polymer, as suggested in the inset of Fig. 7.

It is also observed that, in addition to the dependence on the humidity and the contact force, the dimensions of the swollen features are also influenced by the duel contact time (longer times allow more molecules diffusing into the polymer), and by the application of an external electric field (for voltages in the 0 to 5 V range the height of the features vary at ~ 1 nm/V).

Fig. 7 PEN working mechanism. An tapered stylus (~ 20 nm apex radius) coated wth acid is used as a source of hydronium ions H3O+. As the probe is brought into contact with the surface, a water meniscus is formed, which acts as a bridge that facilitates the transport of ions towards the sample surface. The applied force facilitates the penetration of the ions into the polymer matrix; upon diffusion the ions protonate the pyridine groups. The inset suggest that the Coulomb repulsion between the protonated pyridine groups results into a net swelling. This working principle also implies that, upon de-protonation the swelling process can be reversed.

Since the protonation can be counteracted by adding a chemical base, the swelling mechanism can then be made reversible. The latter feature stimulates further the development
of PEN since it opens a newer nanofabrication method for biotechnology applications (possibly for creating on/off switching gates, that would allow manipulating the transport, separation, and detection of bio-molecules; the latter occurring in soft-material scaffolds that mimic closer natural bio-environments).

III.2 Sample preparation: Immobilization of polymer films to flat substrates

III.2A. Piranha-cleaning

Silicon wafers with their native oxide layer are cut into square pieces (~ 2cm × 2cm), and subsequently cleaned either by sonication in isopropyl alcohol for 15 minutes. Alternatively the samples are cleaned by immersion into piranha solution (3:7 v/v ratio of H₂O₂ and concentrated sulfuric acid H₂SO₄) for 60 min at 80 °C. For this latter process, organic solvents are kept away from the piranha solution since they reacts violently. First, hydrogen peroxide H₂O₂ is poured into a beaker and then the H₂SO₄ is added slowly. The mixing is very exothermic and steam will be visible; if boiling signs are noticed, it would mean the pouring is going too fast. The pieces are then washed thoroughly with boiling deionized water for 90 minutes and then dried (ideally under a stream of nitrogen). This cleaning procedure creates a surface rich in functional (-OH) hydroxyl groups on the oxide surface, which facilitate the subsequent process (described below) that uses functionalized molecular-glue to covalently attach a polymer film to a silicon oxide substrate.

III.2B Immobilization of the polymer film via PFPA molecular glue

Spin coating is the most popular method to prepare polymer thin films on flat substrates; but the physisorption character of this attachment makes the film prone to easy removal. It is highly desirable to develop more robust film immobilization methods that can make them withstand harsh environmental and processing conditions. Dr. Yan’s group, at the University of Massachusetts Lowell, has developed versatile “double-side” molecular “glue” that is just one monolayer thick for covalently immobilizing a variety of molecules (including polymers, carbohydrates, and electronic materials such as graphene) to a variety of substrates (oxides, metals, and semiconductors). When applied to polymers, this method produces films ~6 nm in thickness after activating of the molecular glue with uv light (but avoiding wavelengths smaller than 280 nm to minimize polymer crosslinks). Additional details of the PFPA covalent attachment process are provided below as a preparation for the route envisioned for the outgrowth of the PEN technique described in Section IV.

a. Monolayer-thick PFPA molecular glue

A general approach for covalent immobilization of polymer films to a silicon oxide substrate uses a family of penta-fluorophenyl compounds that are doubly functionalized with azido and silane groups. The silane group attaches to the substrate and the azido group attaches to a polymer molecule.

i) The functionalization of penta-fluorophenyl compounds with the azido group (containing three nitrogen atoms) is to exploit the ability of nitrogen to get inserted into the C-H covalent bonds of polymer strands upon uv activation. This first functionalization step produces perfluorophenyl azides PFPA (see Fig. 8a).
The functionalization with a silane group (Si atom connected with other four functional groups), as shown in Fig. 8b, is to exploit its reactivity with, and thus covalently attach to, hydroxyl groups (-OH) found on a silicon oxide surface. \textsuperscript{102,103} For completeness, it is worth mentioning that detailed arrangement of silane molecules at the Si/SiO interface has been studied by IR spectral analysis. \textsuperscript{104} Exploiting this reactivity, a variety of silane groups are widely used to form self-assembled PFPA monolayers. \textsuperscript{37,105}

Further details concerning the preparation of perfluorophenyl azides PFPA can be found in references 98 and 99. Preparation of silane functionalized PFPA is described in Refs. 92 and 93.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{Synthesis of molecular “glue” containing a reactive nitride group $N_3$ (which attach well to molecules containing C-H bonds, i.e. polymers, by undergoing C-H and/or N-H insertion reactions upon uv-light activation), and a silane group SiY\textsubscript{4} (which attach well with hydroxyl groups that are present on a piranha-cleaned silicon oxide). a) Synthesis of functionalized perfluoro-phenyl azides (PFPA) from their corresponding pentafluorophenyl. \textsuperscript{98} b) Synthesis of PFPA-Silane 1. \textsuperscript{106}}
\end{figure}

\section*{b. Functionalization of silicon oxide surface with monolayer-thick PFPA-silane}

A piranha-cleaned wafer (with its native oxide and hydroxyl \textendash;OH groups) is soaked in a toluene solution of PFPA-silane (5 mM) for about 4 hours at room temperature. The procedure is performed in sealed vials to minimize contact with air moisture. Subsequently, the wafers are removed from the solution, rinsed with a gentle stream of toluene, dried under nitrogen, and allowed to cure at room temperature for at least 24 hours. \textsuperscript{99}

Figure 9 shows a suggested model of the molecular arrangement that silane groups undergo near the proximity of a silicon oxide surface. The initial density of Si-OH groups is important to establish the final Si-O-Si link arrangements. \textsuperscript{104} Ellipsometry measurements reveal PFPA layer thickness in the 6Å to 11Å range, depending on the soaking time (1 hour to 24 hours). \textsuperscript{101}
c. Immobilization of polymer films on a PFPA-silane functionalized surface via either UV light or thermal activation

Once a PFPA-silane monolayer is attached to a substrate, the azido groups become exposed to the C-H bonds of the polymer molecules that are subsequently added via a spin coating procedure. Polymers in a proper solvent (toluene for polystyrene PS, chloroform for poly(2-ethyl-2-oxazoline) PEOX or for poly(4-vinylpyridine) P4VP) at typically 10 mg/mL solution concentration are spin coated at 2000 rpm for 60 seconds. The initial formation of thick layers (> 30 nm) are purposely attempted (to minimize the eventual formation of voids). The samples are then blown dry with nitrogen and are ready for the subsequent UV irradiation step.\(^93\) A medium-pressure mercury-vapor lamp (450 W power, Hanovia) is used to trigger C-H and/or N-H insertion reactions at the PFPA-polymer interface. (A long pass 280 nm filter is used to protect the polymer from crosslinking caused by very short wavelengths).\(^93\)

A minimum time of 3 minutes of UV-irradiation is required to immobilize the polymer film, (the thickness grows rapidly in the first 5 minutes, and no variation occur after 20 minutes).\(^93\) The final thickness (~ 2-5 nm) is independent of the starting thickness of the film right after the spin coating, which supports the argument that only the polymer molecules in the neighborhood of the PFPA azido group participate in the reaction. The latter result suggest that, if the process were performed at higher temperatures (thus allowing the polymer molecules to explore more spatial configurations and, hence, more frequently exposed to the azide groups on the surface) the efficiency of the C-H and N-H insertion reactions would increase. Indeed, that turns out to be the case. In the absence of UV radiation, just heating the spin coated polymer in an oven at temperatures in the range of 140 to 180, similar immobilization results
are obtained. The formation of a polymer film, involving the insertion of N into the C-H polymer bonds is schematically described in Fig. 10.

![Fig. 10 Schematic description of the attachment of the PFPA azido (nitrogen) groups to polymer molecules. Reprinted with permission from [L. Liu et al, J. Am. Chem. Soc. 128, 14067; 2006]; copyright 2006 American Chemical Society.](image)

**III.2C Polymer films fabrication via uv-activation of crosslinks with uv light (< 280 nm)**

The azido PFPA-silane functionalization method described above is suitable to immobilize monolayer-thick polymer films to silicon oxide surfaces. When thicker polymer layers are required there exists a relatively simpler alternative method that comprises spin coating the polymer and subsequent uv light irradiation to generate crosslinks within the polymer matrix (no molecular glue is required). This method renders films of thickness ranging from a few nm to 80 nm depending on the initial polymer concentration, molecular weight, and irradiation time, which turns out to attach well not only on oxides but also on metallic surfaces. In this process, after spin coating a polymer-solvent solution (10 mg/mL) on a clean surface, irradiation with uv light (mercury lamp, 10 mW/cm² intensity at the sample's surface, no long pass filter used in this case) for 20 minutes is sufficient to strongly attach the film. The medium-pressure Hg lamp has a 222-367 nm spectral emission with a maximum at 366 nm. For testing purposes, when using a 280 nm long pass optical filter no polystyrene film remains after extraction with toluene, which indicates high-energy deep uv light (< 280 nm) is responsible for the immobilization of the films. The film is robust since it remains on the surface after the unattached polymer is removed by extensive extraction with the solvent. Even after after 30 minutes of continuous boiling the film survives. Since the procedure occurs in oxides as well as metal substrates, the working mechanism has been attributed to a crosslinking process.

For the PEN applications we have consistently used poly(4-vinylpyridine) (P4VP). A 10 mg/mL solution of P4VP (Mw ca. 160,000) in CH₂Cl₂ is spin-coated onto the piranha-cleaned silicon wafer at 2000 rpm for 60 seconds, which yield films of thickness in the range of 50 to 80 nm, as revealed by ellipsometry measurements. The film is irradiated with a 450 W medium-pressure Hg lamp at ambient conditions for 5 minutes. The light intensity of the lamp, measured by a sensor with peak sensitivity at 254 nm, is 12 mW/cm² at the sample-plane. (The 5 minute irradiation time includes a 2 minute warm-up for the lamp to reach its full intensity.)
unbound polymer is removed by soaking the sample in CH₂Cl₂ for 24 hours to give the cross-linked P4VP film. The thickness of the film was measured with a Gaertner ellipsometer (model L116A, with a 2 mW He/Ne laser at an incident angle of 70°), assuming a refractive indices 1.465 for SiO₂ and 1.581 for P4VP in the final estimations.

III.3 PEN top-down approach

The PEN nanoscale patterning process constitutes an extension of previously reported swelling of UV-crosslinked P4VP large-area films under acidic stimulation. In that experiment, measurements performed before and after soaking cross-linked P4VP films in a pH 4 buffer solution indicated a 20% increase in the films’ thickness (measured by ellipsometry of the dried films), while a shift in the (IR-spectra) frequency-band, associated to the pyridyl ring-stretching modes, provided a signature of the protonation. The increase in film thickness is attributed to the protonation of pyridyl groups, caused by the added acidic component to form pyridinium ions, whose mutual repulsions cause the film to expand (see the inset in Fig. 7). Triggering the polymer swelling mechanism via the delivery of acid through a sharp stylus, as outlined in Fig. 7 establishes a new way to create nanostructures. Here we outline the necessary instrumentation and typical procedure.

Atomic force microscopy (AFM) system with scanning lithography capabilities: Currently we use an AFM IX-20 model from Park Scientific, which controls the vertical position of the probe (a cantilever with pyramid-shape tip at one end, as shown in Fig. 7) while being laterally moved, in a raster fashion, along the sample’s surface. The system is able to control the force that the tip exerts over the sample, as well as to establish an electrical potential difference between the sample and the tip (when using metalized probes and metallic substrates.) In a typical procedure, a first step constitutes to test the lithographic capability of the system by creating patterns via scratching a soft polymer film with the silicon tip. Fig 11 shows ‘UNI’ and ‘VALQUI’ patterns written at ambient conditions. Both were “written” in contact mode using an n-type silicon tip (MikroMasch, NSC15, with the top side coated with aluminum to increase the reflectivity of the AFM laser system), a probe-sample contact force of 1.8 µN, and writing speed of 100 nm/s. For the regions where not writing was performed (i.e. going from one letter to the next) a velocity of 5 µm/s and 80 nN (i.e. less contact force). In the case of the VALQUI pattern the writing force was changed to 1250 nN. The reason for the decrease was to prevent excessive accumulation of polymer on the tip during the process, since the writing length was doubled with respect to the first pattern.

Preparation of the acidic fountain tip. A source of hydronium ions H₃O⁺ is prepared out of phosphate buffered solutions, which have the remarkable property that can be diluted and still keep the same concentration of H₃O⁺. Different pH values can be obtained by dissolving corresponding quantity ratios of sodium dihydrogen phosphate (NaH₂PO₄) and sodium hydrogen phosphate (Na₂HPO₄) in distilled water. For example, mixing 13.8 g/l and 0.036 g/l of the two salts, respectively, gives 0.1 M buffer solution of pH equal to 4.0. This acidic solution serves as the source of hydronium ions. Subsequently an AFM tip of relatively high spring constant (k = 40 N/m) is coated by simply soaking the probe into the buffer solution for about 1 minute (Fig. 7a) and then allowing it to dry in air for 10 minutes or, alternatively, by blowing it
with nitrogen (Fig. 7b.) Such fountain tip constitutes the probe for delivering hydronium ions very locally over targeted sites on a responsive material substrate.

**Pattern Fabrication.** The experiments described below used as starting material to 50 nm thick P4VP polymer film fabricated by crosslink activated by uv radiation (*i.e.* no PFPA molecular glue was used).

i) First, the atomic force microscope (AFM), with the “ink” loaded tip, is set in “tapping imaging-mode,” in which the cantilever probe undergoes oscillations perpendicular to the sample’s surface. To obtain an initial knowledge of the “blank paper” (a UV cross-linked P4VP polymer film), an image is taken at a relatively fast lateral scanning rate of 6 µm/s (0.5 Hz line scan rate, 6 µm line width, 100 pixels per line). It is found that the use of such modest high rates prevent the transfer of buffer molecules into the substrate.

ii) Once it is verified that the scanned area is free of unwanted topographic features, the AFM microscope is switched to “contact imaging-mode” for patterning formation under physical parameters controlled by the operator, namely contact forces of the order of 1 µN, ‘writing’ speeds up to 400 nm/sec (0.05 Hz line scan rate), and fixed bias voltages up to 5V. Patterns of different planar morphologies can be generated with pre-programmed software designs, which guide the voltage-controlled XY lateral scanning of the tip while an electronic feedback-control
keeps the probe-sample contact force constant. In our case, using a Park Scientific AFM IX-20, the sample rests on a XY piezo scanner stage (equipped with strain-gauge sensors for overcoming piezoelectric hysteresis via another internal feedback control\(^{43}\)), while the tip is held by an independent piezoelectric z-stage. This is a convenient way of decoupling the sample’s horizontal XY scanning motion from the probe’s vertical z-displacements, which avoids potential mutual “cross talk” between the lateral and vertical motion of the tip.

\(\text{iii})\) Finally, once the pattern process is completed, the AFM microscope is switched back to the tapping mode for topography imaging in order to verify whether the patterns have been formed.

Figure 12 shows schematically a sequential process of the pattern formation, as well as a 3D view of an actual line-pattern created exploiting the responsive characteristics of P4VP. The cross-linked film swelled only in the area where the phosphate “ink” was intended to be delivered by the scanning probe while applying a contact force \(F\) of 1500 nN and a bias voltage \(V\) of +5 Volts. The experiment was performed at ambient condition (local humidity of 60%). It is widely accepted that a ~ 20 nm thick layer of water (and other potential contaminants) is present on the surface of any sample at ambient conditions. The image demonstrates the ability for sequentially creating an initial pattern (while scanning the probe in contact mode) and then imaging (in tapping mode) the resulting sample topography with the same ink-loaded tip.

\[\text{Fig. 12 Top-down PEN patterning with responsive polymers.}\] The diagram shows the process at different length scales. \(a\)) Fabrication of a 50 nm thick film of macro-scale dimension area (cm dimension). \(b\)) Creation of fine structures using a sharp stylus (apex of ~ 20 nm) loaded with acid “ink”, and scanned across the sample surface in contact mode under a pressing force and a bias voltage. Swollen features of desired lateral morphologies are created as protons are transfeffed from the probe’s tip to the substrate. \(c\)) Imaging of the resultant pattern in tapping-mode imaging modality using the same ink-loaded tip.
The line profile in Fig. 13 reveals that the line-feature is approximately 25 nm in height and 500 nm in width. This height represents a 50% local increase in thickness, a substantial swelling that reveals the hydrogel characteristics of the pattern. A hydrogel refers to a flexible (typically) hydrophilic cross-linked polymer network and a fluid filling the interstitial spaces of the network. The entire network holds the liquid in place thus giving the system a solid aspect. But contrary to other solid materials, these wet and soft systems are capable of undergoing very large deformation (sometimes greater than 100%). Hence, the hydrogel-type structures fabricated via PEN with P4VP constitute an advantage of the technique for replicating structures that closely mimic natural bio-environments. Indeed, the role of gels in living organism cannot be exaggerated. As it is well put by Osada and Gong,110 living organisms are largely made of gels (mammalian tissues are aqueous materials largely composed of protein and polysaccharide networks,) which enables them to transport ions and molecules very effectively while keeping its solidity.

![Image of line profile and top view of line feature](image)

**Fig. 13 Hydrogel characteristics of the pattern.** Top view and line profile of the line-feature created via PEN with a 50 nm thick P4VP polymer film as starting material. The substantial swelling of the feature reveals the hydrogel characteristic of the pattern, which is suitable for creating structural environments that mimic closer natural biological environments.
The dimension of the PEN patterns is influenced by the environmental humidity. By increasing humidity, one expects an increase in size of the water meniscus around the tip, and hence an increase in the amount of the hydronium ions ink that can be transported from the tip towards the sample’s surface. PEN pattern formation in P4VP films under different humidity levels has been well documented by C. Maedler. Dot-like structures were created by keeping the probe in contact with the sample during different dwell times and at different relative humidity inside of the chamber containing the AFM system. By starting at 60% RH and subsequent continuous decrease of the RH, dots were written at 60%, 50% and 40% RH, respectively. No structures could be created for RH below 30%. The results are summarized in the graph in Fig. 14. The formation of no features below 40% of relative humidity suggests that the transfer of the buffer molecules from the tip to the surface requires a sufficient water meniscus between tip and sample. Buffer molecules probably dissolve in the water before diffusing into the P4VP polymer. Without dissolution no molecules can be transferred to the substrate. With decreasing RH the height of the structures decreases, which indicates that the water meniscus becomes smaller.

A smaller water meniscus leads to fewer dissolved buffer molecules and therefore a lower rate of protonation of the pyridyl groups.

Fig. 14. Humidity dependence on pattern formation a) Dot-like structures form by leaving the acid-coated tip in contact with the substrate for different amounts of time. The dwell time is indicated above the peaks. b) Pattern height against dwell time and relative humidity. No pattern were possible to create below 40% humidity. Reprinted from (C. Maedler et al, Proc. SPIE, 7364, 736409-1, 2009), and reproduced with permission of the SPIE.

The fabrication process is also affected by the force that the tip exerts against the surface as well as by the application of an electric field between the silicon tip and the silicon substrate (see setting in Fig. 12b). This has been well documented by Xiaohua Wang, whose results are summarized in Fig. 15. The experiments were performed at ambient environment 23-26°C and 45-55% relative humidity. Notice that the application of a bias voltage alleviates the need of applying stronger forces (the latter could damage the polymer). For a 5V bias voltage, structures can be fabricated with forces as small as 0.5 μN, which otherwise wouldn’t
be able to be created. We attribute the applied voltage helps to drive the hydronium ions into the polymer matrix; when a negative voltage is applied to the probe no patterns are formed. Typical bias voltages are up to 5 V, which when applied through a 50 nm film sets a strong electric field $\sim 10^6$ V/cm (still leaving the film apparently undamaged.) Provided that the humidity is above 40%, the patterns are consistently fabricated with this PEN method. On the other hand, the application of a force appears to facilitate the insertion of the hydrogen ions into the polymer matrix. Although the high humidity facilitates the transport of the ion from the tip to the surface, at the same time it may cause the ions to diffuse along the sample surface. A gentle indent of the probe into the substrate may create a channel for the ions to get immersed into the polymer matrix and diffuse towards the pyridine center of the P4VP molecules.

![Fig. 15. Force and bias voltage dependence on the pattern formation](image)

(a) Pattern height (nm) vs. applied bias voltage (V) at various fixed contact forces. (b) The pattern height (nm) vs. applied contact forces ($\mu$N) under different constant bias voltages. Reprinted with permission from [Xiaohua Wang et al, ACS Appl. Mater. Interface 2, 2904; 2010], copyright @ 2010, American Chemical Society.

Although the results given above favor the hypothesis of protonation, would the hydronium ions be the only ones diffusing into the polymer network? To test this hypothesis C. Maedler et al investigated further the swollen structures. Armed with Kelvin Probe Force Microscope as a tool, and following up studies of deposition of charges in silicon, Maedler et al corroborated to have the sensitivity for monitoring the presence of a net charge in the polymer structures, if any. But they found none on the P4VP polymer films. This implies that not only the hydronium ions penetrate the polymer, but they bring with them their corresponding counterions (see expression below) thus keeping the charge neutrality of the sample. If the fixed pyridinium cations were the only ions present there would be an exceedingly large electrostatic repulsion, but such interaction is partially screened by the presence of counterions resulting from the dissociation of the phosphate salts in water,
Here $K$ stands for the corresponding dissociation constants.

\[
\begin{align*}
\text{NaH}_2\text{PO}_4 & \rightarrow \text{Na}^+ + \text{H}_2\text{PO}_4^- \\
\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-} \quad K = 6.31 \times 10^{-8} \\
\text{HPO}_4^{2-} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{PO}_4^{3-} \quad K = 3.98 \times 10^{-13}
\end{align*}
\]

**IV Bottom-up Proton-fountain Electric-field-assisted Nanolithography (PEN):**

Self-assembly fabrication of nanostructures with responsive characteristics

The PEN top-down approach described in the previous section offers a convenient platform for fabricating mesoscopic (hydrogel-type) stimuli responsive structures with fine precision. Such an ability to control the dimensions of patterns with 1 nm per volt precision is suitable, for example, to study the size-dependence properties of these structures. But to go beyond the study of fundamental properties and consider massive device production, both the fabrication speed and the still relatively thick dimension of the patterns are issues that need to be addressed in order to make the PEN technique competitive with other nanofabrication techniques. In effect,

i) PEN nanostructures are currently fabricated one at a time in a serial fashion and at a speed of 400 nm/sec, which is too slow by commercialization and industrial applications standards.

ii) The patterns lateral dimension is limited by diffusion. Basically, upon their injection into the polymer matrix, the hydronium ions naturally diffuse towards the pyridine centers of the P4VP matrix (then the mutual repulsion of these centers causes the polymer to swell). It is the lateral diffusion, then, what limits the creation of narrow features. Even though features with 60 nm line-width have been created with this top-down approach, better control to create finer line-width features would be desirable.

This section explores strategies to overcome these two limitations. Essentially, we propose to use a fabrication procedure based on the self-assembly of P4VP molecules onto a surface that has been previously chemically-functionalized with high resolution. On one hand, a self-assembly approach would inherently assure a fast and massive fabrication procedure (provided that the chemical functionalization is also fabricated by a fast method). On the other hand, pre-functionalizing the substrate with high lateral resolution would ensure the attachment of responsive polymer material only to pre-determined well-localized sites; hence when exposed to an acid bath the diffusion of the hydronium ions would be intrinsically avoided. In addition, given the reversibility of the P4VP swelling, the nanostructures could be erased upon immersion in a base-chemical bath. In short, we pursue the design of chemical functionalization methods that can be implemented with high resolution and ideally also at very fast pace. Ultimately we envision fast method for fabricating erasable nanostructures.

Addressing the high-resolution and speed fabrication aspects, this section is organized as follows. The first part of this section outlines a general view of some thermal and optical routes available for the chemical functionalization of a substrate with high resolution. For the optical route, conventional (far-field) and near-field illumination modalities are considered. The far-
field option is included for its additional capability to undertake the chemical functionalization at fast pace (when implemented with very short-pulse illumination and exploiting non-linear thermal material responses). The near-field option offers high resolution although its scanning implementation limits its fabrication speed; still different near-field illumination strategies could render the technique very useful. Here far-field refers to conventional optics where the sample is illuminated through a lens located at a distance greater than the wavelength; hence the name ‘far-field’. Near-field refers to a setting where the sample is illuminated through a ~100 nm aperture located at a distance much smaller than the wavelength from the sample; hence the name “near’ field; see Fig. 17. The second part offers a background on the working principles behind the highly localized thermal effects produced by the incidence of femtosecond laser pulses on a material. The high-gradient temperature profile produced by mechanic/thermal contact is also mentioned. This background helps to put into context the suggested bottom-up implementation of PEN. The third and fourth parts describe in more detail the implementation of the high resolution chemical functionalization.

**Fig. 16** Schematic (macroscale) procedure for covalent attachment of polymer molecules to a surface functionalized with PFPA monolayer “glue”. (1) The silane group reacts with the native SiO2 built on the silicon wafer substrate thus forming a self-assembled monolayer. (2) Polymer is spin coated. (3) Upon (thermal or uv) chemical activation, perfluorophenyl nitrenes are generated and undergo C-H and/or N-H insertion reactions with neighboring polymer molecules; a polymer coating is formed. In a nano-scale approach, the attachment of polymer molecules at more localized sites can be achieved by implementing step 3 using far- and near-field optical tools (as outlined in Fig. 17).

**IV.1 High spatial resolution chemical functionalization**

The new strategies proposed here for the outgrowth of the PEN technique build upon the covalent-immobilization techniques described in section III.2B above, particularly the attachment of polymer films to a silicon oxide surface. One of those methods uses PFPA as a monolayer-adhesive sandwiched between the substrate and the polymer film; while the PFPA’s
silane group attaches to the sample surface and (under either ultraviolet-radiation or thermal activation) the PFPA’s azido group grabs a polymer molecule in the film (as outlined in Figs. 10 and 16).99

The variation to be introduced in this fabrication process lies in step-3. By integrating high spatial and temporal resolution optical techniques it would be possible to engineer the functionalization of PFPA (and the P4VP molecules) on well-localized sites on a sample substrate (Fig. 17a):

- One option is to illuminate the sample in a far-field modality with very short pulses (750–840 nm, 9.5 nJ per pulse, 25 fs pulse duration) in order to establish high-gradient temperature profiles on the substrate that is in intimate contact with the PFPA layer. An expected Arrhenius-type temperature dependence of the PFPA chemical activation (~$Ae^{-E/kT}$) implies that the thermal gradient could produce a more localized chemically activated PFPA region compared to the illuminated region. In other words the laser power can be selected so that only a small section of the Gaussian diffraction-limited focus exceeds the required intensity to trigger the chemical reaction. This short-pulse illumination method would inherently lead to high lateral resolution. The far-field implementation is for attaining a fast fabrication process since the illuminated spot can be rapidly scanned using resonant mirrors.114,115

![Fig. 17 Schematic description of a self-assembly method for fabricating nanostructures using stimuli-responsive P4VP molecules.](image)

**Fig. 17** Schematic description of a self-assembly method for fabricating nanostructures using stimuli-responsive P4VP molecules. **a)** **High-resolution opto/thermal PFPA functionalization of the substrate.** Sample is illuminated through a conventional (far-field) objective lens with femtosecond pulses to establish non-linear thermal absorption on the substrate. The thermal gradient produces a more localized chemically activated region of the PFPA layer than the illuminated region; hence the higher resolution. Alternatively, the sample is irradiated through a sub-wavelength aperture using a near-field probe (see also Fig. 18). A scanning of the sample relative to the optical probes allows high resolution pattern features. **b)** **After sonication, a functionalized surface results.**

**c, d)** **Self-assembly organization of stimuli-responsive P4VP molecules.** In step c) the functionalized surface is spin coated with, or simply immersed into, a solution of P4VP; a far-field optical activation leads to a covalent attachment of the P4VP molecules to the PFA centers. **d)** After toluene extraction, only the P4VP molecules covalently attached to the surface remains. Notice the more localized illumination approaches allow attempting the immobilization of P4VP down to, potentially, single molecules.
Fig. 18 Sequences of the fabrication of a Near-field optical probe. A. Optical image of a commercially available optical fiber glass (120 µm cladding, 8 µm core diameter) that has been tapered via chemical etching. B. SEM-image of an aluminum coated fiber glass probe. Since the conditions for total internal reflection in the fiber has been spoiled in the tapered region, the metal coating is to prevent the leakage of light and channel the light coupled at the back of the fiber towards the apex region. C: A focused ion beam is used to carefully truncate the apex of the probe thus leaving an aperture.

・ Another option is to illuminate the sample with uv-light through an apertures of sub-wavelength dimension (using a near-field probe like the one shown in Fig. 18), provided that the aperture is placed very near the surface (~ 10 nm) to avoid diffraction; hence the name “near-field” illumination. This method offers high resolution implementation.

It would be interesting to establish a systematic comparison between these two opto/thermal covalent activation methods for immobilizing PFPA molecules onto a substrate. Harnessing the functionalization of a surface with PFPA is key for the success of the project, for the remaining PEN fabrication steps would become straightforward: the post self-assembly attachment of the stimuli-responsive P4VP molecules onto the PFPA centers will simply require a spin coating process or, even simpler, jut dipping the functionalized substrate into a solution containing P4VP molecules (Fig. 17).

In the following sections we describe in a bit more detailed the two far-field and near-field optical approaches to chemical activation. But first we provide some background on the highly localized thermal effects on materials produced by very short pulses in order to provide the context underlying the proposed high-resolution chemical functionalization techniques.

IV.2 Highly spatially-localized thermal effects
Highly localized thermal effects on materials are associated with femtosecond pulses excitations as well as with nonlinear thermal responses as a result simple contact with heated probes. In this section we briefly outline these two aspects.
IV.2A Localized thermal ablation effects produced by femtosecond pulses

The remarkable highly spatially-localized thermal effects produced by ultra-short (sub picosecond) laser pulses was evidenced in the initial experiments of polymer ablation in 1987. Pulses of 160 fs etched holes on polymethylmethacrylate (PMMA) with sharp edges and no sign of collateral thermal damaged. Thermal diffusion was absent and there was virtually no solid deposit of the polymer at the sides of the hole. The interpretation, however, followed some controversial discussions. Since PMMA has negligible absorption at 308 nm wavelength the result was initially attributed to multi-photon excitation. But experiments in 2003 ruled out this hypothesis on the basis that the optical breakdown is independent of the light polarization. Additional explanation would surface later on.

Previous to these experiments, the accepted principle was that laser-induced electron avalanche ionization (where electrons with a sufficiently high energy cause ionization in successive collisions, thus creating a new generation in the avalanche) as the mechanism that determines the breakdown threshold in pure transparent crystalline or amorphous solids and liquids. Once sufficiently dense plasma has been created, the joule heating losses in the strongly colliding electron gas become so large that internally localized melting and/or evaporation takes place. The surrounding matrix may be subsequently damaged by shock waves induced by thermal stresses. The new paradigm brought by excitation with short pulses is that sub-picosecond duration time is significantly shorter than the time scale for electron energy transfer to the lattice. As a result, damage caused by sub picosecond pulses is characterized by ablation, with essentially no collateral damage.

But what produces the first initial seed for avalanche ionization to take place? The question is daunting since multi-photon excitation has already been ruled out. A clue comes from the remarkable feature that more deterministic ablation breakdown thresholds are obtained when using femtosecond laser, which contrast with the more random ablation thresholds measured when using longer pulses; that is, ablation thresholds measured from place to place along the material is more uniform when using short pulses. For example a row of holes created in the surface of Corning 0211 glass by single femtosecond pulses (at 527-nm wavelength, average pulse energy of 7.5 nJ, and focused by a 1.3 NA objective on the distal side of the cover slip) displayed a striking reproducibility in size. Such reproducibility in the size of the features combined with the fact that each hole was of nanometer- scales indicates that the initial charge carriers that seed for avalanche-ionization must has been created in a very reproducible manner. It is surprising it had occurred in a heterogeneous material such as glass, in which the band gap varies considerably from spot to spot. Pre-existing carriers cannot explain such uniformity, since the ablation of holes of such small scale (< 20 nm) and sharp edges (~4 nm) with regularity and precision would require initial free-electron densities far higher than present in large-band-gap materials (an electron density in excess of 10^18 e/cm^3 would be necessary to ensure at least one seed electron in the volume of a hole). The multi-photon excitation had also been ruled out. Such pre-existent carriers would vary then randomly along the sample, subjected to a Boltzmann statistics; different threshold energies may occur then at different sites, just because this random effect. An accepted explanation for the reproducibility of the features is that when using femtosecond pulses then the tunneling (Zenner effect) of electrons from the valence band become more effective to contribute as initial seeds due to the high electric fields; the uniformity of the valence-electrons population is then attributed to be
responsible for the uniformity of the ablated regions. In short, an accepted trend of thought is that the deterministic character of the optical breakdown is dictated by the material valence-electron spatial uniformity; in good-quality optical material the energy gap may vary substantially over small scales but the valence-electron density, which is proportional to the atomic density, is extremely uniform.\textsuperscript{119}

Another important feature to take away from these experiments is that the deterministic breakdown threshold (producing sharply ablated features) and the Gaussian intensity profile of a laser pulse (exponential variation of the light intensity) implies an exponential dependence of the size $D$ of the breakdown zone on the pulse energy. Joglekar et al reported\textsuperscript{119} that $D = \sigma \sqrt{8 \ln \left( \frac{E}{\nu} \right)}$, where $D$ is the diameter, $E$ is the pulse energy, and $\nu$ and $\sigma$ are fitting parameters: $\nu$ gives the threshold ablation energy. One could extrapolate from these results an exponential dependence of the local temperature established by the fast-pulse excitation, which gives indication on the high-gradient temperature gradient that can be exploited to activate chemical reactions by adjusting the experiment to use lower incident power.

**IV.2B Modification of physical properties by sub-picosecond pulses**

In addition to the very localized ablation of hard materials by sub picosecond pulses,\textsuperscript{119,123} there exists also evidence of their effects on just the chemical structure modification of polymer films (i.e., with no ablation). In one case, for instance, the fast excitation process led to a change in the film’s wettability properties even though there were not changes in the film’s roughness (the other possible channel for changing the film’s wettability properties).\textsuperscript{124} The non-linear absorption of fs laser pulses was ascribed to photo-degradation, distinct from the thermal-degradation associated with linear absorption when using wider (ns) pulses\textsuperscript{125}. The short (fs) pulses allowed reaching power absorption threshold-limits for increasing concentrations of C=O polar bonds (over the non-polar C-O bonds), hence the modification of the film’s wettability properties. On the other hand, control of the fs pulse energy can avoid material ablation and still causing changes in the material’s physical properties. For example, (20-50 nJ) pulses with energy levels below the ablation threshold where use to locally increase the refractive index on fused silica, the irradiated regions also developing lower thermal conductivity. Such results have been interpreted in terms of a localized densification of the regions exposed to the fs pulses.

**IV.2C High-resolution chemical activation via high-gradient temperature profiles**

Spatially-confined activation by high temperature gradients has been put into evidence by Cacialli et al,\textsuperscript{126} using a setting where a heated stylus is laterally scanned while in mechanical contact with a soluble polymer film, poly(p-xylene tetrahydrothiophenium chloride)(PXT). It was known that this precursor polymer can be turned into insoluble poly(p-phenylene vinylene) (PPV) upon the application of ultraviolet radiation at the selected places, thus providing an avenue for creating patterns. It turns out that a heated stylus could equally work well. What is surprising in this work is that, despite the blunt morphology of the stylus, nanometer-sized PPV patterns could be created. These results have been explained in terms of the high temperature gradient on the sample and the strong temperature-dependence of the PXT-to-PPV reaction rate. With a perspective of large scale production, a potential drawback of this approach is that the “writing” tip, being in intimate mechanical contact with the polymer sample, would be
subjected to contamination; the scanning process could be detrimental to samples constituted by monolayer films (causing scratches) and impose restriction on the writing speed. As an alternative, we propose establishing high temperature gradients through a far-field illumination of the substrate (stylus-sample mechanical contact is avoided), as indicated in Fig. 17a. In short we will pursue high resolution PFPA functionalization using a far-field optics approach to establish a gradient temperature on the underlying substrate.

**IV.3 Thermal activation of PFPA molecules with femtosecond pulses**

The above background helps to put in context the proposed ideas for implementing PEN in a top-down approach, which can now be simply listed.

**IV.3A Far-field approach to attain high-gradient temperature profiles on the substrate**

An avenue to achieve high resolution chemical functionalization of PFPA monolayer is by establishing high temperature gradients on the underlying glass or silicon substrate using far-field illumination optics. As shown in Fig. 17a, fs laser pulses are employed to create nonlinear absorption on the silicon substrate. The non-linear process on the substrate, under conditions below ablation threshold, should render a local high-gradient temperature profile to activate the PFPA very locally. Although not shown in the figure, an added advantage of this far-field optical setting is that the illuminated spot can be rapidly scanned using resonant mirrors.\(^{114,115}\)

![Fig.19](image)

**Fig.19** Local activation of PFPA molecules with high lateral resolution by exploiting high-gradients temperature profiles using femtosecond pulses. The spot is scanned in two dimensions with the use of a galvanometer mirror (GM) and a resonant galvanometer mirror (RGM).\(^{115}\)

**IV.3.B Local heating activation with a near-field probe**

Alternatively one can use metal-coated near-field probes to locally heat the sample. The apex of a NSOM probe (Fig. 18) reaches temperatures well above the ambient conditions depending on the light intensity coupled into it. Placing the apex at a nanometer distance from the PFPA monolayer (under feedback electronic control) the local high temperature at the apex (~250°C) could activate the PFPA molecules located underneath (see Fig. 17b and Fig. 20). A systematic control to heat the probe was first reported in 1995\(^{127}\) Shortly after, Stähelin et al. established that the axial temperature distribution at the probe apex was non-uniform.\(^{128}\) The
temperature at the apex of the probe was estimated to be 100 °C when 1 mW input power was coupled into the back of the fiber holding the probe. Coupling 3.3 mW of laser light into the fiber resulted in a maximal temperature of 230 °C at the apex. This temperature range is well within the range of temperatures at which PFPA is thermally activated (as described below), which it can be exploited to create patterned polymer nanostructures by thermal activation. This feature is attractive and important especially for polymers such as isotactic polypropylene and poly(ethylene glycol) where heat treatment is essential for successful film immobilization.129

Fig. 20 Heat effects on a NSOM probe. a) Schematic of a probe of tapered geometry. b) Closer to the apex, the probe’s inner cross-section area gradually becomes too narrow for sustaining the light’s propagating modes, but evanescent modes are allowed, whose energy is deposited within the skin-depth of the inner metal interface. c) The apex of the probe is placed in the proximity of the sample. The application of pulses of light can be used to control the probe temperature and, hence, locally thermally excite the PFPA monolayer.

Fig. 21 Immobilized film thickness as a function of temperature. Reprinted with permission from M. Yan and J. Ren, Chem. Mater. 16, 1627 (2004). Copyright 2004 American Chemical Society.

Studies of PFPA activation at macroscopic scales by thermal means has been reported.94 For a 5 minute heating time, the thermal activation of the surface azido groups occurred only at temperatures above 140 °C (see corresponding open squares in Figure 21). Below this temperature, no film immobilization occurred. Accordingly, when using a metal-coated near-
field probe, setting the peak temperature at its apex above, the thermal activation temperature of the azido groups, film immobilization should take place only in the region around the area at peak temperature, thus minimizing line broadening. It will be interesting to determine the temperature at which optimal spatial resolution can be achieved without compromising the integrity of the immobilized films. In short this approach would constitute a near-field thermal excitation, exploiting the gradient temperature established on the metallic probe.

IV.3.C The ultraviolet near-field approach

Radiation from a Ti:Sapphire laser system (equipped with non-linear optics for doubling and tripling the operating fundamental frequency at $\lambda = 790$ nm) can be coupled to sub-wavelength apertures, which when scanned in the proximity of the sample trigger the PFPA reaction at predetermined localized sites. This is the realm of near-field uv-lithography. Different types of sub-wavelength sized apertures can be used for this near-field uv application, including metallic apertures fabricated at the apex of tapered fiber glass probes (as the ones shown in Figs. 18 and 20 above); apertures fabricated (using a focused ion beam) at the pyramid-apex of a semiconductor atomic force microscope probe; or apertures fabricated out of GaAs, which latter displaying extraordinary transmission efficiency (due to the intrinsic nature of the uv radiation).

In near-field uv-optical lithography, light that exits the sub-wavelength aperture (laterally scanned in close proximity, 10 nm, to the sample surface) induces chemical reactions very effectively in the surrounding materials via polymerization, crosslinking, or decomposition. Distinct irradiated regions, scanned over with the near-field optical probe, can subsequently be etched out by capitalizing on the differential solubility of the exposed and unexposed regions, thus creating nanometer-sized structures. The experimental protocol will start by treating silicon wafers with PFPA-silane. The sample will then be scanned with a near-field probe. PFPA-silane has a maximal absorption at 256 nm that tails to 350 nm. The un-attached polymer will be removed by soaking the sample in a solvent. Exposure time will be optimized to investigate the attainable resolution of a given near-field probe. The spatial resolution and the topography of patterned films will be characterized using AFM as well as near-field optical microscopy. A number of parameters will be investigated with respect to spatial resolution, immobilization yield and film integrity. These include the aperture size of the probe, tip-sample distance, intensity of the UV laser, and scan rate.

IV.4 Implementation

We will explore PFPA chemical activation via non-linear thermal response of the surrounding substrate using femtosecond laser pulses. The non-linear response (absorption of multiple photons) is associated to the high power intensities resulting from the incidence of pulses of short duration, which results in an intrinsic spatial confinement effects because of the high temperature gradients. While confined effects are reported in the context of material ablation applications (features of 20 nm have been fabricated using radiation of 527-nm wavelength, average pulse energy of 7.5nJ). We certainly will not seek material ablation, but instead study the nonlinear absorption effects for chemical bond modification.
VI. REFERENCES


A hydrogel refers to a flexible (typically) hydrophilic cross-linked polymer network and a fluid filling the interstitial spaces of the network.


http://www.gitam.edu/eresource/nano/nanotechnology/role_of_bottomup_and_topdown_a.htm


http://www.mtl.kyoto-u.ac.jp/english/laboratory/nanoscopic/nanoscopic.htm


C. Maedler, “Applying different modes of atomic force microscopy for the manipulation and characterization of spatially localized structures and charges,” Diploma Thesis for the academic degree of Diplom Physiker; Faculty of Natural Sciences Institute of Physics, Chemnitz University of Technology (2009).

A functional group is a specific group of atoms within a molecule that is responsible for characteristic chemical reactions of that molecule. The hydroxyl group is a functional group consisting of a hydrogen atom covalently bonded to an oxygen atom.


Hiroyuki Sugimura, “Self-assembled monolayer in silicon” http://www.mtl.kyoto-u.ac.jp/groups/sugimura-g/PDF/SAM-on-Si.pdf A molecule consisting of one Si atom connected with four functional groups, SiX₄, is called as “silane”. If one, or more, of these functional groups are substituted with organic functional groups (X=CH₃ for example) it is called organosilane. Organosilane molecules react with hydroxyl groups on an oxide surface.


109 Since all phosphate salts are used in hydrated condition, the molecular weight (MW) should include the corresponding portion of water. For NaH2PO4 we should include one molecule of water, hence the MW is 137.99. On the other hand, for the Na2HPO4 we should consider 7 molecules of water (heptahydrate,) which gives a MW of 268.07. Hence, if 13.8 g and 0.036 g of NaH2PO4 and Na2HPO4 are used respectively, then we can quote the concentration of NaH2PO4 (the buffer strength) to be practically equal to 0.1M.


