Nanolithography on Responsive Materials
Proton-fountain Electric-field-assisted Nanolithography (PEN)

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In memoriam
Sailaja Chada
Nanolithography on Responsive Materials

Proton-fountain Electric-field-assisted Nanolithography (PEN)

I. Motivation: Underlying emerging biomimetic engineering
PEN as a method for creating erasable nanostructures using responsive materials

II. Comparison between “PEN” and “Dip pen nanolithography”

III. Fabrication procedure
   III.A Preparation of P4VP responsive material
   III.B Preparation of acidic fountain tip

IV. Underlying working mechanisms of swelling in hydrogels
The osmotic pressure. Lattice model for calculating the entropy: Ideal liquid vs Polymer solutions.
Pattern formation in responsive polymer films triggered by local protonation

Polymer film preparation

Silicon wafer (“Piranha” cleaned)

Spin coated P4VP film (uv-cross-linked)

acridic phosphate buffer

$\text{H}_3\text{O}^+$

AFM probe $k = 40 \text{ N/m}$

Patterns formation on soft materials

Pattern formation in responsive polymer films triggered by local protonation
Responsive materials
Respond to a stimulus (mechanical, chemical, optical, changes in environmental conditions, etc.)


One current focus in biomimetic materials
Development of versatile synthetic responsive thin films

➢ In one approach, the complex synthetic hierarchy (needed to mimic natural bio-systems) is conceived as a combination of domains separated by stimuli-responsive thin films that regulate the interactions between the domain compartments.

Underlying emerging biomimetic technologies

- In another approach, a cell is conceived not just as a chemical but also as a mechanical device. It is found that the cell membrane is very sensitive to the mechanical properties of its surrounding matrix (affecting their growth, differentiation, migration, and, eventually, apoptosis.)


Both approaches emphasize the need for harnessing the fabrication of synthetic thin film responsive materials.
Underlying emerging biomimetic technologies

Top-Down and Bottom-up approaches

Research on biomimetic materials have resulted in the design of a variety of responsive building blocks: hydrogels, brushes, hybrid systems with inorganic particles that respond selectively to pH, temperature, optical, and magnetic external stimuli.

Following the “bottom-up” route: self-assembly of polymeric supramolecules.

Progress using “top-down” approach: responsive polymer brushes, growth of polymers from DPN-patterned templates, chain polymerization triggered by local stimulation using a STM stylus.
Underlying emerging biomimetic technologies
Top-Down and Bottom-up approaches

PEN falls in the top-down category approach.

Atomic force $\rightarrow$ Dip pen $\rightarrow$ PEN

microscopy nanolithography

Our description concentrates on hydrogels, since the latter describes closer the experimental results obtained in current applications of PEN.
Hydrogels,
A flexible (typically) hydrophilic cross-linked polymer network and a fluid filling the interstitial spaces. The entire network holds the liquid in place thus giving the system a solid aspect.
Contrary to other solid materials, these wet and soft systems are capable of undergoing very large deformation (greater than 100%).
Atomic force microscopy → Dip pen nanolithography → PEN

Allows controlling the probe-sample distance

Deposition of molecules

Molecules deposited on the substrate constitute the patterns

Water meniscus

The locally triggered swellings of the substrate constitute the pattern

Probe (‘pen’)
Dip pen nanolithography

Deposition of molecules ("ink")

Probe ('pen')

Substrate ('paper')

Nanopatterned Ink

http://mcf.tamu.edu/instruments/dip-pen-nanolithographer
Dip pen nanolithography

Deposition of molecules ("ink")

‘Ink’ molecules deposited on the substrate constitute the pattern

http://mcf.tamu.edu/instruments/dip-pen-nanolithographer
Pattern formation in responsive polymer films triggered by local protonation

**Swelling mechanism**

Coulomb repulsion between the pyridinium ions leads to an increase of the film thickness.

P4VP Polymer
Pattern formation in responsive polymer films triggered by local protonation

Silicon wafer (“Piranha” cleaned)  
Spin coated P4VP film (uv-cross-linked)

Acidic phosphate buffer

AFM probe $k = 40 \text{ N/m}$

‘Pen’ preparation

Polymer film preparation (soft material)

The locally triggered swellings of the film constitute the pattern
Preparation of polymer thin films

**Immobilization by direct UV Irradiation**

- Robust attachment
  - Scotch tape test
  - Boiling solvent
- Ease of preparation
- Substrate-independent

1) Coat polymer
2) UV irradiate
3) Solvent extract

Polystyrene

Crosslinking

\[
\begin{align*}
\text{Polystyrene} & \quad \rightarrow \quad \text{crosslinking} \\
\text{chain scission} & \quad \rightarrow \quad \text{chain scission}
\end{align*}
\]

Oxidative Degradation

Poly(4-vinyl phenol)

Thin films stimuli-responsive Characteristics: Evaluation

- large response
- fast
- reversible

Pattern formation in responsive polymer films triggered by local protonation

Pattern formation in responsive polymer films via local protonation

A. La Rosa and, M. Yan, in “Tip Base Nanolithography” (to be published in June-2011)

Sequential fabrication and imaging

Writing: rate = 0.04 line/s; i.e. 100 nm/s or 1 pixel / 250ms
Imaging: rate = 2 line/s; i.e. 5 µm/s or 1 pixel / 5ms
Role of humidity

Effect of Electric Field and Contact Force

PEN
Finest line structures

PEN Reversibility

Underlying working mechanisms of swelling in hydrogels

Chemical potential of water in phase-A (pure solvent water) is greater than the chemical potential of water in phase-B (solvent + solute)

A. La Rosa and M. Yan, in “Tip Base Nanolithography” (to be published in June-2011)
Underlying working mechanisms of swelling in hydrogels

Gibbs free energy $G = G (T, P, N)$.

Being the temperature $T$ and pressure $P$ intensive quantities, $G$ has to have the form

$$G = N f(T, P),$$

where $N$ is the number of particles of the analyzed system.

Since $dG = -S \, dT + V \, dP + \mu \, dN$ and $\mu = (dG/dN)_{T,P}$, the extensive property $G = N f(T, P)$ implies that $\mu$ is only a function of $T$ and $P$; that is,

$$\mu = G/N = f(T, P).$$
Underlying working mechanisms of swelling in hydrogels

Accordingly, $\mu$ is the Gibbs free energy per molecule, and it is a quantity independent of $N$. Thus,

$$d(G/N) = d\mu = - \left( \frac{S}{N} \right) dT + \left( \frac{V}{N} \right) dP,$$

which implies,

$$\frac{d\mu}{dP} = \frac{V}{N}.$$
Underlying working mechanisms of swelling in hydrogels

This expression is pertinent to the quantification of the osmotic pressure. In effect, it reflects the change in chemical potential due to an increase in pressure, $\Delta \mu = (V/N) \Delta P$ (where it has been assumed that the volume does not change with pressure.) Using $\nu \equiv (V/N)$, one obtains

$$\mu_{\text{water}, P_2}^B - \mu_{\text{water}, P_1}^A = \nu (P_2 - P_1),$$

$$\mu_{\text{water}, P_2}^B - \mu_{\text{water}, P_1}^A = \nu \Pi_{\text{osmotic}}$$