Scanning Probe Nanolithography

- STM - early work
- Arranging atoms with a tip
- Local Oxidation Lithography (Electrochemical)
- Dip Pen Lithography
- Nanografting

Recent Topical Review:
STM-based Results
Writing nanometer-scale symbols in gold using the scanning tunneling microscope

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65 nm x 40 nm x 2 nm
D. Eigler moves and controls position of an individual Xe atom (1989)

35 Xenon atoms on Ni(110)

Physical Mechanism

a) Adsorbate atom interacting with substrate

b) Approach tip; adsorbate atom interacts with tip and substrate

c) Drag adsorbate atom to new location

d) Withdraw tip
Local Oxidation Lithography

Early Work:

Upon approach, a water neck forms. Due to surface tension, an additional force is required to pull the tip from the substrate. The additional force depends on the shape \((r_1, r_2)\) of the water meniscus.

\[ p = \text{partial pressure } H_2O \]
\[ p_0 = \text{ambient pressure} \]
\[ \text{RH} = \frac{p}{p_0} \]
Water layer adsorbed on quartz at room temperature

Water layer adsorbed on $\text{SiO}_2$ at room temperature

**SPM Oxidation Lithography - Schematic**

a) non-contact, feedback ON

b) Feedback OFF
   -30 V pulse for ~20 msec

Typically RH 30% - 40%

establish water neck

c) Feedback OFF
   -20 V for ~2 sec

d) non-contact, voltage OFF; feedback ON

oxidation chemistry
Local Chemistry at the Tip

1. Si rapidly reacts with oxygen to form passivating layer of SiO₂

\[ Si + O₂ → SiO₂ \]

2. Water vapor also oxides Si; (gaseous O₂ is not required)

\[ Si + 2H₂O → SiO₂ + 2H₂ \]

3. Large electric field dissociates water

\[ H₂O \xrightarrow{large \, E} OH^- + H^+ \]

4. OH⁻ diffuses through SiO₂ faster than O₂, allowing the oxide to grow

\[ \text{SiO}_2 \]

\[ \text{Si} \]
Examples - Local Oxidation Lithography

S.W. Howell, Sandia National Labs

P. Ares, Nanotec Electronica
Minimum Feature Size

Estimating the height:

\[ h \sim \left( \frac{t}{t_0} \right)^{\gamma} \]

\[ \gamma \sim 0.1 - 0.3 \]

\[ t \sim 0.005 - 1 \text{ s} \]

Local Oxidation enables fabrication of:

a) Dielectric barriers
b) Masks for selective etching
c) Templates

Chemical Writing
"Dip-Pen" Nanolithography
Richard D. Piner, Jin Zhu, Feng Xu, Seunghun Hong, Chad A. Mirkin*
Nanolithography with Molecules

Lateral force images of Au substrate; RH 35%

Piner, Zhu, Xu, Hong, Mirkin, Science 283, 661 (1999)
Fig. 1. Nanoscale molecular letters written on an Au(111) surface with MHA molecules by DPN.

Hong, Zhu, Mirkin, Science 286, 523 (1999)
As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord’s Prayer on the head of a pin. But that’s nothing; that’s the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2060, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

Richard P. Feynman, 1960
Nanografting

Early Work:

Self-Assembled Monolayers

Self-Assembled Monolayers (SAMs) are ordered molecular assemblies formed by the adsorption of an active surfactant onto a solid surface.


Molecules that can form a SAM (schematic):
The Self-Assembly Process

Initial adsorption

Lying-down Phase

Transition from lying-down to standing phase

Standing-up phase

~5 - 10 hours
Nanografting

Self-assembled monolayer

Two nanografted spirals, 620 nm in diameter, with average line spacing of 40 nm, average line-widths (FWHM) of 15 nm, and average heights of 0.15 nm. Mono-atomic steps in Au(111) are clearly present.

Summary
Mechanisms to Modify Surfaces