Nanostructured Materials - Fabrication Processes

FABRICATION PROCESSES FOR NANOMATERIALS - NANOSTRUCTURES

Lecture 6
SUBTRACTIVE AND MODIFYING METHODS

- **Subtractive methods:**
  - Etching: wet chemical etching, reactive ion etching, ion beam sputter etching.
  - Tool-assisted material removal: chemical-mechanical polishing, chipping, drilling, milling, sand blasting.
  - Radiative and thermal treatment: laser ablation, spark erosion.

- **Modifying methods:**
  - Radiative treatment: resist exposure, polymer hardening.
  - Thermal annealing: crystallization, diffusion, change of phase.
  - Ion beam treatment: implantation, amorphization.
  - Mechanical modification: plastic forming and shaping, scanning probe manipulation.
FIB milling

• Sputter process.
• Resolution better for small current but high currents mill faster - use series of decreasing currents.
• Significant redeposition - milling strategy is important.

• High depth of focus (ion shorter wavelength than electron) – non-flat surface OK.
• Coupling with SIMS (secondary ion mass spectrometry) can give in-situ information on chemical content.

Charging effect when milling insulator

FIB milling without (left) and with (right)
Charge neutralization (courtesy FEI Company)

Charging can be eliminated by electron beam bombardment of surface. (most FIB is equipped with SEM for imaging and charge neutralization)
Nanostructured Materials

Channeling effect when milling crystalline material

Box milling of poly crystalline material (steel), rough surface.

Box milling of poly crystalline Cu.

Channeling effect suppressed by doping with impurity atoms that block the ion channels.

State-of-the-art: 3nm!

NanoFIB

20 nm thick membrane (dose: one spot of 106 ions, image sizes 50 x 50 nm)
**FIB implantation and pattern transfer: results**

Nano-cup by extending vertical FIB milling to several μm.

SEM photomicrographs of cantilevers (2μm long, 100nm wide and 30nm thick).

Tseng, "Recent developments in nanofabrication using focused ion beams", Small, 1(10), 924-939 (2005).

**LITHOGRAPHY USING CHARGED PARTICLES: FIB**

- Ga⁺ ion beam (down to 5nm) to raster over the surface.
- FIB can cut away (mill, sputter) material (electron is too light for this).
- By introducing gases, FIB can selectively etch or deposit a metal or oxide.
ADDITIVE METHODS

Thin film deposition
• Physical vapor deposition (PVD): sputtering, e-beam or thermal evaporation
• Chemical vapor deposition (CVD): metal-organic CVD, plasma-enhanced CVD, low pressure CVD...
• Epitaxy: molecular beam epitaxy (MBE), liquid-phase epitaxy...
• Electrochemical deposition: electro- and electroless plating (of metals)
• Oxidation (growth of thermal SiO_2)
• Spin-on and spray-on film coating (resist coating)

Printing techniques: ink-jet, micro-contact printing
Assembly: wafer bonding, surface mount, wiring and bonding

PROCESS OF TRANSFERRING PATTERNS TO MATERIALS IN ANALOGY TO PHOTOGRAPHIC PROCESS

LITHOGRAPHY
APPLICATIONS OF NANOLITHOGRAPHY

Advantages
- High resolution
  - Precise manipulation of single molecules
- Inexpensive compared to similar high resolution techniques
- Imaging capabilities allow real-time manipulation
- Can be performed in ambient conditions (including fluids)

Disadvantages
- Currently a serial process
- Scanner nonlinearities

NANOLITHOGRAPHY

· Solid-state nanoresists
· Cryptography
· Ultra-small, -sensitive, and -selective sensors
· Nano- and microfluidics
· Molecular electronics (organic, bio-organic circuits)
· Crystallization (colloidal crystals, biostructures)
· Nanoprinted catalysts
· Ultrahigh density oligonucleotide arrays (gene chips, sequencing)
### Lithography – general distinction

#### Lithography with particles or waves
- Photons: photolithography
- X-rays: from synchrotron, x-ray lithography
- Electrons: electron beam lithography (EBL)
- Ions: focused ion beam (FIB) lithography

#### Imprint lithography (molding)
- Soft Lithography: micro-contact-printing...
- Hot embossing
- UV-curable imprinting

#### SPM-lithography
- AFM
- STM
- DPN (dip-pen nanolithography)

#### Pattern replication: parallel
(masks/molds necessary)
- High throughput, but not easy to change pattern
- Optical lithography
- X-ray lithography
- Imprint lithography
- Stencil mask lithography

#### Pattern generation: serial
(Slow, for mask/mold making)
- E-beam lithography (EBL)
- Ion beam lithography (FIB)
- SPM-lithography
  - AFM, STM, DPN

#### Multiple serial (array)
- Electron-beam micro-column array (arrayed EBL)
- Zone plate array

### Resolution will depend on wavelength

#### Lithography on surfaces
- Optical/UV lithography
- E-beam lithography
- FIB lithography
- X-ray lithography
- SPM-lithography
  - AFM
  - STM
  - DPN (dip-pen nanolithography)

#### Lithography in volume
- Two photon absorption
- Stereo-lithography

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**Pattern replication:**
- Parallel: (masks/molds necessary)
  - High throughput, but not easy to change pattern
- Serial: (Slow, for mask/mold making)

**Pattern generation:**
- E-beam lithography (EBL)
- Ion beam lithography (FIB)
- SPM-lithography
  - AFM, STM, DPN

**Multiple serial (array):**
- Electron-beam micro-column array (arrayed EBL)
- Zone plate array
**OPTICAL LITHOGRAPHY**

- Light sensitive resist
- Silicon Wafer

- Expose to UV light
- Exposed region becomes more soluble and the pattern is reproduced on the resist layer
- Underlying semiconductor material etched by acid
- Solvents remove resist

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**NANOLITHOGRAPHY**

- Metal nanostructures
- Substrate

- Direct etch process
  1. Thin film growth
  2. Lithography
  3. Etching
  4. Etching (dissolve resist)

- Liftoff process
  1. Thin film growth
  2. Lithography
  3. Deposition
  4. Etching (dissolve resist)
Electron Beam Lithography and Nanofabrication

Exposure

Bilayer e-beam resist structure. A high molecular weight PMMA is spun on top of a slightly more sensitive bottom layer of low molecular weight PMMA.

Development

The resist is developed in MIBK:IPA giving an undercut.

Metal deposition

Liftoff

The resist is removed in a liquid solvent leaving the pattern.

CR NANODOTS BY LIFTOFF

Pitch: 200nm

1. Cr dots by liftoff
2. RIE silicon and remove Cr (RIE: reactive ion etching)

70 nm diameter

35 nm diameter

115 nm diameter
HIGHER RESOLUTION LITHOGRAPHY

X-Ray – 1-1.5nm range
lack of refractive x-ray optics

Extreme UV Lithography
10-14nm wavelength

Nanosphere lithography

1. drop coat spheres
2. assembly into monolayer
3. deposit metal
4. perform lift-off

Colloidal crystal mask
Ag Nanoparticles
THE ELECTRON BEAM LITHOGRAPHY

Types of EBL

1. Electron Beam Direct Write
2. Electron Projection Lithography

APPLICATIONS OF ELECTRON BEAM LITHOGRAPHY

• Research
  - Nanopatterning on Nanoparticles
  - Nanowires
  - Nanopillars
  - Gratings
  - Micro Ring Resonators
  - Nanofluidic Channels

• Industrial / Commercial
  - Exposure Masks for Optical Lithography
  - Writing features
NANOPATTERNING ON NANOPARTICLES

Significance
- Photonic Crystals
- Quantum Dots
- Waveguides

Electron Beam Lithography
- Fine writing at moderate electron energies
- 37nm thick lines with 90nm periodicity
- 50nm diameter dots with 140nm periodicity

NANOWIRES
EBL with Electrochemical size reduction
- Widths approaching 10nm regime

Patterning of Films of Gold Nanoclusters
- Sub 50nm wide Nanowires
- Controlled thickness at single particle level

NANOFIUIDIC CHANNELS
- Laboratory on a chip
- Single Molecule Detection
- Tubes with inner dimension of 80nm


(2005) A single step process for making nanofluidic channels using electron beam lithography, J. L. Pearson and D. R. S. Cumming
NANOPILLARS

EBL and Reactive Ion Etching
- Etched Pillars with 20nm diameter

Nanotechnology using Electron Beam Lithography, Center for Quantum Devices

GRATINGS

Lithography using charged particles I: electron beam lithography (EBL)

Finely focused electron beam, $\phi = 2$-$5$ nm

Resist (PMMA...)

develop resist

evaporate metal

perform lift-off

Metal patterning by EBL and liftoff
ELECTRON PROJECTION LITHOGRAPHY

Electron Beam Direct Write

Electron Projection Lithography

New solutions

Limited throughput

Huge penetration depth of electrons

SCALPEL (Bell Laboratories and Lucent technologies) 1995
PREVAIL (IBM) 1999

RESIST LIMITATIONS

PMMA often

Tendency of the resist to swell in the developer solution.

Electron scattering within the resist.

- Broadens the diameter of the incident electron beam.
- Gives the resist unintended extra doses of electron exposure.
Processing Rate vs. Lithography and Its Best Resolution

- Photolithography: 3 billion years
- E-beam lithography: 30 years
- AFM lithography: 25 hours
- STM lithography: 1/100 sec
- Processing time for 5x5 mm²: 1/10,000 the area single Si wafer

Scanning Probe Lithography (SPL)

- Mechanical patterning: scratching, nano-indentation
- Chemical and molecular patterning (dip-pen nanolithography, DPN)
**AFM LITHOGRAPHY - SCRATCHING**

(SIMPLEST, MECHANICAL LITHOGRAPHY)

- Material is removed from the substrate leaving deep trenches with the characteristic shape of the tip used.
- The advantages of nano-scratching for lithography
  - Precision of alignment, see using AFM imaging, then pattern wherever wanted.
  - The absence of additional processing steps, such as etching the substrate.
- But it is not a clean process (debris on wafer), and the AFM tip cannot last long.

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**SPL**
Scanning Probe Lithography

**AFM**
Manipulation of nanostructures

**STM**
Manipulation of atoms/molecules
SURFACE MANIPULATION WITH AFM

- Surface manipulation of colloidal gold on mica
- Data storage
- Sensors
- Single electron transistors


- Manipulation of Nanotubes
- Single molecule logic circuit

DIP-PEN NANOLITHOGRAPHY

A tiny speck of gold positioned between two parallel carbon nanotubes forms a transistor that forwards one electron at a time. These single electron transistors could be used to make extremely small, low-power logic circuits.

Source: Land University

Solid Substrate
Surface Science (DPN)
DIP-PEN NANOLITHOGRAPHY (DPN)

- Similar to micro-contact printing, and writing using a fountain pen.
- AFM tip is “inked” with material to be deposited
- Material is adsorbed on target
- <15nm features
- Multiple DPN tip arrays for higher throughput production

EXAMPLES OF DPN INKS INCLUDE THIOLS, ANTIBODIES, POLYMERS

- Thiol ‘Ink’ on gold (Friction Image)
- Chemical ‘Ink’ on glass (Confocal Images)
- Electroluminescent polymers
- Tagged antibodies
- Human Hair (80 μm width)
SCANNING TUNNELING MICROSCOPY - STM

TIP
ATOM
TUNABLE BOND
SURFACE

CRYSTALLINE SURFACE
Iron atoms where arranged on a copper surface to make the kanji character for “atom”

Carbon Monoxide Man consisting of carbon monoxide molecules on a platinum surface

IS SMALLER BETTER ALWAYS BETTER

As soon as I mentioned 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 2000, when they look back at this age, they will wonder why it was not until the year 1950 that anybody began seriously to move in this direction.

Richard P. Feynman, 1950
ANODISING

ANODIZED ALUMINUM OXIDE TEMPLATES

- Aluminum
- Nanoporous aluminum oxide (AAO)
- Anodization Acid Bath (oxalic, sulfuric, or phosphoric acid)
- Counter electrode

~ 40 V
I

e.g., • Keller, et al., J. Electrochem. Soc. 100, 411 (1953)

Masuda, et al.
Rapid anodic oxidation of highly ordered TiO$_2$ nanotube arrays

Yan Wang$^{a,b}$, Yucheng Wu$^{a,*}$, Yongjiang Jin$^a$, Gaobin Xu$^a$, Xiaoye Hu$^a$, Jiwei Cui$^a$, Hongmei Cheng$^a$, Yu Hong$^a$, Xinfu Zhang$^{a,b}$

Fig. 3. High-magnification SEM images of TiO$_2$ nanotube arrays with a diameter of 240 nm and anodized in an electrolyte of oxalic acid and phosphoric acid for 30 min. The nanotube arrays show a smooth and uniform surface with a dense structure. Insert: (a) An optical microscope image of a TiO$_2$ nanotube array, showing the uniform distribution of the nanotubes. (b) A high-magnification SEM image of a TiO$_2$ nanotube, showing the nanotube walls with a smooth surface. (c) A cross-sectional SEM image of a TiO$_2$ nanotube array, showing the uniform thickness of the nanotubes.

Fig. 4. (a) Schematic diagram of the experimental setup for the growth of TiO$_2$ nanotube arrays. (b) Cross-sectional view of TiO$_2$ nanotube arrays in the electrolyte solution. (c) Mechanism for the formation of TiO$_2$ nanotube arrays.
NANOCOATINGS
SOME WAYS OF MAKING THEM
Nanostructured Materials - Fabrication Processes

**PVD**

- No surface diffusion
- Everything sticks where it hits (physical processes only)
- Poor surface coverage
- “Line of sight”

**CVD**

- Precursors diffuse on surface
- Leads to more uniform coating

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**Metal CVD Processes**

Mo, Ta, Ti, Ni, and W are widely used.

- These metals can form useful silicides when deposited onto silicon.

Mo, Ta and Ti are deposited by LPCVD, from their pentachlorides.

Ni, Mo, and W can be deposited at low temperatures from their carbonyl precursors.
**ATOMIC LAYER DEPOSITION (ALD)**

*Coat complex, 3-dimensional objects with precise, conformal layers*

*ALD uses alternating, saturating reactions between gaseous precursor molecules and a substrate to deposit films in a layer-by-layer fashion.*

*By repeating this reaction sequence in an ABAB... fashion, films of virtually any thickness, from atomic monolayers to micrometer dimensions, can be deposited with atomic layer precision.*

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Reaction A, the substrate surface is initially covered with hydroxyl (OH) groups. The hydroxyl groups react with trimethyl aluminum (TMA) to deposit a monolayer of aluminum-methyl groups and give off methane (CH₄) as a byproduct.

Because TMA is inert to the methyl-terminated surface, further exposure to TMA yields no additional monolayer.
Case Study:
Development of High Performance “Nanostructured” Ternary Nitride Coatings, and Assessment and Modelling of Their Performance

Coatings were deposited in a Varian 3120 deposition unit.

Pirrani gauges and Tylan mass flow controllers were used to monitor pressures and flow rates of reactive gas.

Coatings with multiple-layers of Ti/TiAl/TiAlN or Cr/CrAl/CrAlN were produced.
**NANOINDENTATION PROPERTIES**

Mechanical properties of the coatings determined by nanoindentation

<table>
<thead>
<tr>
<th>Nitrogen Pressure (mTorr)</th>
<th>0.40</th>
<th>0.96</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness, H (GPa)</td>
<td>18.6 (1711)</td>
<td>13.6 (1251)</td>
</tr>
<tr>
<td>Elastic Modulus, E (GPa)</td>
<td>264</td>
<td>196</td>
</tr>
<tr>
<td>Plasticity Parameter, $\delta = \varepsilon_p / \varepsilon$</td>
<td>0.53</td>
<td>0.51</td>
</tr>
</tbody>
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**COATING ON DRILLS**
SOL GEL

Sol-Gel Technologies and Their Products

LIMITATIONS

Graph showing weight/area (ng/cm²) vs. withdraw speed (cm/min) with different sols indicating cracks.
SPIN COATING

DIP COATING