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Those slides summarized several research projects I carried out at National Research Council (NRC) during 2003-2008

## Nanostructure Fabrication by Nanoimprint Lithography and its Applications

Bo Cui CNRC-Industrial Materials Institute



Conseil national de recherches Canada

National Research Council Canada



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## Outline

#### **Part I: Introduction**

What is nano? Why nano? How to reach nano? Micro and nano-fabrication: lithography, etching, thin film deposition One example of nanofabrication

#### Part II: Nanoimprint lithography (NIL) (hot embossing)

Hot embossing of several materials

- Polystyrene (biocompatible)
- Poly(lactic-co-glycolic acid) (biodegradable)
- MEH-PPV (semiconducting polymer for plastic solar cell)
- Metal (pulsed laser melting)

Replication of 100nm to mm-scale features by thermal NIL

#### Part III: Plasmonic chemical/biosensors based on metallic nanostructures

Introduction to plasmon

DNA hybridization detection by surface plasmon resonance (SPR)

Surface enhanced Raman scattering (SERS)

- Raman scattering and SERS fundamentals
- Fabrication of nano-prism array as SERS active substrates
- SERS detection of R6G molecules and peptides
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## How small is nano? **Things Manmade**

## **Things Natural**

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Virus, ~100nm



Ant ~ 5 mm



~50 micron wide



DNA~2 nm diameter

Nano world (1-100nm) Red blood cells ~ 2-5 micron

10<sup>-4</sup> m Micro world 10<sup>-5</sup> m

10<sup>-6</sup> m

10<sup>-7</sup> m

10<sup>-8</sup> m

10<sup>-9</sup> m

10<sup>-10</sup> m

10<sup>-3</sup> m

10<sup>-2</sup> m



Head of a pin 1-2 mm



MicroElectroMechanical Systems (MEMS) 10 -100 micron wide







Intel transistor

Nanorobot

Au nanoparticles 13 nm & 50 nm



Carbon nanotube ~2 nm diameter

Adapted from office of Basic Energy Sciences Office of Science

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## Why go to nano?

## L: length

- Integrated circuit: faster, more function, lower power consumption
- Data storage: higher capacity ( $\infty 1/L^2$ ), 1Tbits/in<sup>2</sup> 25nm×25nm/bit
- Semiconductor: quantum confined phenomena (quantum dots/wells...)
- Magnetism: single domain formation at L<magnetic domain wall thickness, superparamagnetism</li>
- Photonics: new phenomena at L<λ photonic crystal, negative refractive index, near field optics, plasmonics
- Biomedical: DNA sorting (nanofluidics), drug delivery (nanoparticles)
- Chemistry: higher surface area

higher reactivity for catalyst, higher sensitivity for chemical sensors

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## How to reach nano?

Bottom up (chemical): assemble small building blocks (atoms...) into larger structures chemical synthesis, self assembly nanoparticle, nanowire, nanotube... low cost, high resolution (~few nm), 3D (sphere)

Top down (engineering): modify large object to give smaller features lithography, thin film deposition, etching expensive, precise control of size/shape and positioning

Top down approach: three components Lithography: generate pattern in a material *called resist* photolithography, electron-beam lithography, <u>nanoimprint lithography</u> Thin film deposition (growth): spin coating, chemical vapor deposition, molecular beam epitaxy, sputtering, evaporation electroplating Etching (removal): reactive ion etching, ion beam etching, wet chemical etching, polishing

 $\rightarrow$ Semiconductor industry uses top down approach

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## Lithographies: a comparison

Photolithography: *duplicate* pattern on the photo-mask into photo-resist fast, low resolution ( $\sim\lambda$ ), standard for micro-fabrication

Electron beam lithography: generate pattern by serial writing into a resist slow (1 wafer/day), high resolution (~10nm)

Nanoimprint lithography: *duplicate* mold pattern into a polymer resist fast, high resolution (2nm), low cost

 $\rightarrow$ NIL is the choice for nanoscale patterning over large surface area

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## Nanoimprint lithography (NIL)

Thermal NIL (hot embossing lithography) force

- Rigid resist at room temperature (RT).
- Softened and patterned at high T.
- De-emboss at low temperature.
- Simple and low cost resist polymers, for general applications.

**UV-curable NIL** 



- Soft liquid resist, patterned at RT
- Hardened by UV-induced polymerization
- No thermal cycle, targeted for semiconductor industry requiring accurate alignment





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Cr-

## One more step: 200nm period pillar array with various diameters







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### Application: cell-antibody interaction

For a fixed pitch of 200nm

# of antibody a cell interacts  $\infty$  pillar surface area  $\infty$  (diameter)<sup>2</sup>



Goal: study how many antibody molecules are required to activate a cell. Activation represented by the upward slope of the fluorescence curve.

 $\rightarrow$ More antibodies, shorter cell activation time

Collaboration with MIT/Northeastern University (ongoing)



## **Summary for Part I**

- 1. Nano-science studies the length range 1nm-100nm
- 2. New physics and applications appear at nanoscale, or just better performance
- 3. Two approaches for arriving at nano: "bottom up" and "top down"
- 4. Three components for "top down" approach: lithography, thin film deposition and etching.
- 5. Nanoimprint lithography is a molding process having high throughput and high resolution.

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# Hot embossing of polystyrene (biocompatible)



### Application: contact guidance of cell growth

- Definition: anisotropic topographic features induce cells to align along the direction of the anisotropy.
- Importance: in tissue engineering, if tissue is to be repaired, the new cells must be aligned and positioned correctly.

Collaboration with LOEX of Laval University



Journal of Cell Science 116 (10)



- First layer: both cells aligned with the grating (as expected).
- Second layer:

Corneal cells - <u>oriented at 60° relative to first layer, as in a native cornea</u> Dermal cells - no orientation

Guillemette, Cui... Nature Methods, to be submitted

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2µm

70µm-

## Hot embossing of PLGA

(poly(lactic-co-glycolic acid)) (biodegradable, biocompatible)



SEM image of 30µm period PLGA grating (SEM: scanning electron microscopy)

100um

#### **Application:**

Brain repair: grow neuron cells on PLGA gratings and transplant it into brain. The support PLGA will disappear in 1-2 months (as it is biodegradable).

Collaboration with NRC-Institute for Biological Sciences

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# Hot embossing of semiconducting polymers

SEM image of 200nm period MEH-PPV grating





MEH-PPV Tg=65°C. Hot embossing at 120°C and 20bar. MEH-PPV spun on a PEDOT/ITO/glass.

Collaboration with Organic Vision Inc. and McGill University

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## Application: nanostructured plastic solar cell



Classic planar p-n junction, low junction area, low efficiency



Nanostructured junction, high junction area, high efficiency



Layers: glass/ITO/PEDOT/MEH-PPV(p)/Alq3(n)/Al

- Plastic solar cells: flexible, light weight, tunable electrical properties, and potential lower fabrication cost.
- Limitation: low energy conversion efficiency due to low carrier mobility.
- Method to increase efficiency: increase the interface area by nanopatterning the p-n junction.



# "Hot embossing" of metal using pulsed laser



#### Copper grating



- XeCl pulsed excimer laser,  $\lambda$ =308nm,  $\tau$ =20ns, 0.2-0.5J/cm<sup>2</sup>.
- Lines rounded due to surface tension and volume shrinking upon solidification
  - Metals are generally more difficult to pattern due to lack of suitable RIE process (RIE: reactive ion etching)
  - Here Ni and Cu were patterned and the step took only ~100ns with minimal heating of the substrate

Cui..., manuscript in preparation

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## NIL for small features (<10nm)

Press liquid into a nano-hole



- Pressure  $\propto$  1/diameter.
- But for protruded mold features (pillars...), local pressure at the pillar is much higher than average - easy to imprint.



Thermal NIL into PMMA (**10nm** pillar array mold) Chou, J. Vac. Sci. Technol. B, 1997



UV-curable NIL, **2nm** carbon nanotube mold Hua, Nano Lett. 2004

→NIL not difficult for nano, especially for protruded mold features



NIL for large features (>100 μm) simultaneous pattern duplication of large and small features

- Application: large features needed to connect small ones to the outside world (electrodes...).
- Challenge: more polymer must be displaced over longer distances.
- A popular approach: two-step process small features by NIL, large ones by photolithography.
- Previously, pattern size of  $100\mu m$  duplicated by thermal NIL.
- Here, we will demonstrate pattern duplication of nm mm features.

 $\rightarrow$ More challenging to duplicate large features than small ones



Assumptions: periodic mold structure (period 2L) ignore inertial, gravitational forces and surface tension resist film thickness = mold trench depth =  $h_0$ 

$$L = \frac{2h_0}{3} \sqrt{\frac{p\tau}{\mu}} \propto \left(\frac{p\tau}{\mu}\right)^{1/2}$$

L: achievable feature size p: pressure τ: imprinting time μ: viscosity h<sub>0</sub>: film thickness

 $\rightarrow$ Achievable feature size depends on pressure, time and viscosity of molten polymer



# Strategy to imprint large features (mm)

L: achievable feature size

p: pressureτ: melting timeμ: viscosity

For PMMA at T>Tg=105°C (glass transition temperature)

$$\log \mu = n \log M_{w} - \frac{12.21(T - T_{g})}{70.1 + (T - T_{g})} + const$$

 $M_w$ : molecular weight n=1 for  $M_w < M_C$ , un-entangled molecules n=3.4 for  $M_w > M_C$ , entangled molecules

Viscosity for PMMA (M<sub>c</sub>=30kg/mol) a) 12 kg/mol, 200°C b) 12 kg/mol,150°C c) 120 kg/mol, 200°C  $\mu_a:\mu_b:\mu_c=1:126:278$ 

 $\rightarrow$  Use low molecular weight PMMA and imprint at high temperature

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### Square (mm) imprinted into PMMA

Optical image Profile



resist need to etch silicon wafer

Need excessive etch to remove the **thick** resist at the square center

Strategy to imprint large features (mm)

But for nanoscale features...



Such a profile makes liftoff difficult. Solution: use tri-layer resist system



 $\rightarrow$  Need excessive resist etch and tri-layer resist for large features

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RIE:

## **Fabrication process flow**



 $\rightarrow$ Fabrication is liftoff process using tri-layer resist plus etching

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## Result of pattern duplication of nano-grating and mm-square



→For small features, line-width increased by ~18nm (acceptable).
 →For large features, 1.3mm squares faithfully duplicated (one order higher than previously achieved).

Cui..., Microelectronic Engineering, 2006



## **Summary for Part II**

- 1. Hot embossing can pattern various functional polymer materials: biocompatible, biodegradable, semiconducting
- 2. It is not so difficult for NIL to achieve high resolution (<5nm)
- 3. It is more challenging to pattern large features (>100 $\mu$ m)
- 4. We have demonstrated simultaneous pattern duplication of nm to mm-scale feature

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Plasmon: "bulk", surface, localized

Plasmon: *collective* oscillation of free electrons (has nothing to do with *plasma* TV (ionized gas))



Annu. Rev. Phys. Chem 2007

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### Lycurgus Cup of the 4<sup>th</sup> Century

#### **Green = Reflected Light**

**Red = Transmitted Light** 





Image of Ag/Au nanoparticle in the Lycurgus cup

Color is due to *resonant* absorption of light, which excites localized surface plasmon when  $\omega(light) \approx \omega(plasmon)$ 

The British Museum. http://www.thebritishmuseum.ac.uk/ (March 2004)

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## Surface plasmon resonance (SPR) biosensor

SPR: excitation of surface plasmon by light Plasmon frequency is very sensitive to changes on metal surface Application: biosensor (DNA, protein...)



- Excitation of surface plasmon by *evanescent* wave
- Resonant absorption occurs at certain angle  $\boldsymbol{\theta}$
- → SPR sensor detects change in thickness/refractive index on metal surface

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# Enhanced DNA hybridization detection by SPR on periodic Au nano-post array

Au nano-posts increase sensitivity by:

- 1. Coupling between localized (from nano-posts) and propagating (from underlying continuous film) surface plasmon.
- 2. Increasing the surface area for DNA binding.





Collaboration with McGill University

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# Enhanced SPR detection of DNA hybridization



 $\rightarrow$  Sensitivity was enhanced by 5× when post diameter = 50nm

Malic, Cui... Optics Letters, 2007

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## **SERS** (surface enhanced Raman spectroscopy) fundamentals

#### Molecular vibration:

- Molecular vibrational energy quantized (phonon).
- $\succ$  Its frequency lies in infrared (IR) spectral range.
- $\succ$  IR spectroscopy is used to identity a material. (strong absorption when v(photon)=v(phonon))

incident light  $h\nu_{_{aS}}$  $\Lambda\Lambda_{r}$  $_{\Gamma}$  scattered light  $v(photon) = v_0 \pm v(phonon)$ 

Raman scattering:

- > Inelastic light scattering from a sample with a shift in frequency by the energy of its characteristic molecular vibrations (phonon).
- > It detects symmetric vibration, which complements IR spectroscopy.
- > The vibration information is transferred from IR to visible, where brighter sources and more efficient detectors are available.

SERS effect: enormous enhancement (up to 10<sup>12</sup>) of Raman scattering when a molecule is adsorbed on *nanostructured* metallic surface. This arises from two main mechanisms -

Electromagnetic effect (dominant):

localized surface plasmon resonance. (Raman intensity  $\propto E^4$ )

Chemical effect: electronic coupling between molecule and metal.

metal nanostructure



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# SERS advantages, approaches to generate SERS-active surfaces

### Advantage of SERS: (3 "S")

- Sensitivity high, single molecule detection demonstrated
  Selectivity high, fingerprint of each type of molecule
  Speed high, few seconds
- High field at tiny gaps

Metallic particles (chemical synthesis) High field at sharp corners, or tiny gaps if close enough ↓ ↓

#### Metal nanostructure

→Nanofabricated metal structures - tunable resonant wavelength, homogeneous size/shape, more reproducible and reliable SERS detection

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## **One example: nanoprism**

(triangular nanostructure)

#### Motivation:

- Localized surface plasmon resonance can be tuned systematically by varying the size, shape and height of the nanoprism.
- Sharp corners of the nanoprism lead to a strong local electromagnetic field enhancement.

Vertical polarization



High field spots

#### Previous fabrication method:

- Chemical approach: reduction of metal salts (difficult).
- Light-induced aggregation of small nanoparticle seeds (low yield and none-homogeneous)





→Nanoprism: tune plasmon resonance, enhance local electrical field





KOH etch Si (111) direction 100 times slower than other crystalline planes. So etching will "stop" at (111) crystalline plane, forming an inverse-pyramidshaped hole.

Fabrication of mold with inversepyramid-shaped hole array



SEM image of the mold (SEM: scanning electron microscopy)

→KOH etching of *crystalline* Si is anisotropic



## SERS detection of rhodamine 6G (R6G) molecule

#### SEM image of 200nm period nanoprism 60000 Si Raman Intensity (arb. units) 55000 nanoprism array of Cr(2.5nm)/Ag(20nm) 50000 45000 40000 35000 30000 25000 20000 200 800 400 600 1000 1200 1400 1600 1800 Raman Shift (cm<sup>-1</sup>)

#### Raman measurement:

excitation laser  $\lambda$ =785nm, power 0.16mW/mm<sup>2</sup>, beam spot size 25-30 $\mu$ m, collection time 3sec.

 $\rightarrow$ Raman signal from ~monolayer R6G is nearly comparable to that from *bulk* silicon

Cui..., Nanotechnology, 2008



#### Why Cr is detrimental to SERS?

Electric permittivity  $\varepsilon = \varepsilon_1 + i \varepsilon_2$ Strong SERS requires large  $\varepsilon_1$  (strong charge oscillation) and small  $\varepsilon_2$  (low loss) But at  $\lambda = 800$  nm  $\varepsilon_1(Cr)/\varepsilon_1(Ag) = 1/20$   $\varepsilon_2(Cr)/\varepsilon_2(Ag) = 50/1$ 

 $\rightarrow$ Keep Cr adhesion layer as thin as possible (1nm)

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Institut des matériaux industriels Numerical calculation by discrete dipole approximation (to optimize nanoprism dimension)





- For single Ag nanoprism,  $\lambda_{res}$ ~720nm.
- Cr decreases absorption efficiency.
- SiO<sub>2</sub> substrate red-shift  $\lambda_{res}$  by 100nm.
- Thicker Ag decreases  $\lambda_{\text{res}}$
- 2×2 array has higher  $\lambda_{\text{res}}$

Discrete Dipole Approximation (DDA):

- It computes scattering of light by wavelength-scale structures.
- The structure is represented by an array of dipoles located in a regular cubic lattice.
- Advantage: only the domain of interest (the metal nanostructure) is discretized.

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Challenges:

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## SERS detection of biomolecules

H-CRF: SQEPPISLDLTFHLLREVLEM AR A E QLAQQAH S NRKL ME I I

B-CRF: SQEPPISLDLTFHLLREVLEM TK A DQLAQQAH N NRKL LD I A

S-CRF: SQEPPISLDLTFHLLREVLEM TK A DQLAQQAH S NRKL LD I A

Bio-molecules compose of similar repeating units (base for DNA, amino acid for protein), hence their Raman spectra are very similar

Solution:

- Attach a tag molecule to the biomolecule, but no longer label-free
- Collect large number of spectra and do regression date analysis

Application:

Detection of drug (e.g. recombinant proteins) abuse in sports (doping).

H: Human; B: Bovine; S: Sheep;

CRF: Corticotropin releasing factors



Collaboration with NRC - National Institute for Nanotechnology

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### **Regression Data Analysis**

Collected 798 spectra per sample

Partial least-squares regression

- A. Score plot representing the first two principal components.
- B. Contour plot showing the correlation for the three CRFs.
- C. Contour plot for their mixtures ("contaminated" samples).
- D. Contour plot for the three CRFs and their 12 mixtures (B+C).



→ SERS can distinguish bio-molecules, but need collect large number of spectra

Alvarez-Puebla, Cui... ChemMedChem, 2007

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# Other types of nanostructures fabricated by NIL: nano-pyramid

Fabrication principle:





1. Triangular hole array

2. Deposit **thin** film



3. Deposit **thick** film Opening close-up gradually due to lateral deposition

3. Liftoff



Nanoprism 30.0kV 6.9mm x60.0k SE(U) 11/09/2007 10:46

Nano-pyramid (3D)

Nano-prism (2D)

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Fabrication principle: Nanoring (red) defined by edge of nanodisk (blue)



1. Hole array with large undercut

Cr deposition at an angle

2. Deposit Cr to cover hole bottom



3. RIE with lateral etch

## Nano-ring and nano-crescent

200nm ∣**←→**∣



Nano-ring

Nano-crescent



Near field for nano-crescent

Cui..., Microelectronic Engineering 2007; Li, Cui...Nanotechnology 2008

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#### Fabrication principle:



1. Nano-hole array (blue color)



2. Enlarge holes due to lateral etching



3. Nano-stars (red color) formed when adjacent holes touch each other

## Nano-star array









## **Summary for Part III**

- 1. Plasmon is collective oscillation of free electrons
- 2. Three types of plasmon: bulk, surface and localized
- 3. Surface plasmon resonance can be used for biosensors
- 4. We achieved  $5 \times$  higher SPR sensitivity by patterning Au nano-post array on a flat Au film
- 5. SERS is an enormous enhancement of Raman scattering when a molecule is adsorbed on a nanostructured metallic surface
- 6. Using nanoimprint lithography, we fabricated arrays of nano-prism, nano-pyramid, nano-ring/crescent and nano-star.
- 7. We demonstrated SERS detection of R6G molecules, as well as peptides classification.

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- -MIT/Northeastern University: X. Cheng, S. Murthy, M. Toner
- -NINT: R. Alvarez-Puebla, H. Fenniri
- -Organic Vision Inc.: S. Xiao

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