Nanotechnology & Microfabrication

Key Issues to Address

- Microsystems
- Microfabrication Processes
- Nanotechnology
- Polymer-Based Systems
Why Microsystems?

Another way of looking at MEMS – linking different science domains

- Heat
- Fluid flow
- Sound
- Mechanics
- Electricity & Magnetism
- Light
- Biology
- Chemistry
- Quantum Mechanics
MEMS History

- **1960s**
  - 1st Silicon pressure sensor in 1961 (Kulite)
  - 1967 Anisotropic Si Etching (H.A. Waggener et al.)
- **1970s**
  - Stanford Integrated gas chromatograph (Terry, Jerman, Angell)
  - Neural probes Ken Wise at Uof Michigan
- **1980s**
  - 1982 Kurt Petersen’s seminal paper “Silicon as a mechanical material”
  - LIGA (Ehrfeld et al.)
  - Si wafer bonding (M. Shimbo)
  - Polysilicon Surface micromaching process developed at UC Berkeley (Howe, Muller, etc.)
  - HP introduces 1st thermal inkjet printer

MEMS History

- **1990s**
  - SCREAM process (Cornell)
  - Bosch etching introduced
  - Commercial surface micromachined accelerometer (Analog Devices)
  - TI DMD
  - MEMS foundries
  - Electrophoresis microfluidic Lab on chip
  - Optical MEMS boom in late 90’s
- **2000s**
  - Optical MEMS bust in early 00s
Miniaturization

- ENIAC - circa 1947
- HP Jamada - circa 2001

10^8 reduction in cost & size
10^8 increase in performance

Basis for Miniaturization

- Shockley, 1947
- First transistor 1947
- Transistor 90 nm process 1998
- First Microheater 1998

- 10^8 reduction in cost & size
- 10^8 increase in performance

First Microheater 1998

Extending Miniaturization

- Reduced: Size, Weight, Cost
- Enhanced: Mixing, Separations, Quenching

Lead to:
- Distributed Processing
- High Yield Synthesis

Require:
- High Surface Area-to-Volume Ratios
- Microchannel Arrays
- Traditional Engineering Materials

DOE PNNL Micro-Scale Fuel Reformer

Microchannel Arrays (Building Blocks)

DOE PNNL Microreactor

MECS

DOE ARC/OSU Micro-Scale Dehumidifier

Microtechnologies for Energy & Chemical Systems (MECS)
Trends and Terminology

- Miniaturization of products and parts, with features sizes in micrometers (10^{-6} m)
  - *Microelectromechanical systems (MEMS)* - miniature systems consisting of both electronic and mechanical components
  - *Microsystem technology (MST)* - refers to the products as well as the fabrication technologies
  - *Nanotechnology* - even smaller components whose dimensions are measured in nanometers (10^{-9} m)

Types of Microsystem Devices

- Microsensors
- Microactuators
- Microstructures and microcomponents
- Microsystems and micro-instruments
Microsensors

- Device that detects or measures some physical/chemical/biological phenomenon
- Most microsensors are fabricated on a silicon substrate using the same processing as integrated circuits
- Microsensors have been developed for measuring force, pressure, position, speed, acceleration, temperature, flow, and a variety of optical, chemical, environmental, and biological variables

Air bag sensor
Microactuators

An actuator converts a physical variable of one type into another type, and the converted variable usually involves some mechanical action

- An actuator causes a change in position or the application of force
- Examples of microactuators: valves, positioners, switches, pumps, and rotational and linear motors
Microstructures and Microcomponents

Micro-sized parts that are not sensors or actuators

- Examples: microscopic lenses, mirrors, nozzles, and beams
- These items must be combined with other components in order to provide a useful function
Microstructures and Microcomponents

- CMOS Silicon compatible technology
- A DLP™ micro-mirror array likely used in the projector making this presentation possible

Microsystems and micro-instruments

Integration of several of the preceding components with the appropriate electronics package into a miniature system or instrument
- They tend to be very application specific
  - Examples: microlasers, optical chemical analyzers, and microspectrometers
Microsystems and Micro-instruments

- Ink-jet printing heads
- Thin-film magnetic heads
- Compact disks
- Automotive components
- Medical applications
- Chemical and environmental applications
- Other applications
**Ink-Jet Printing Heads**

- Currently one of the largest applications of MST
- Today's ink-jet printers have resolutions > 1200 dots per inch (dpi)
  - This resolution converts to a nozzle separation < 20 μm, certainly in the microsystem range

**Compact Disks**

- Important commercial products, as storage media for audio, video, and computer software
  - Mass-produced by plastic molding of polycarbonate
- The molds are made using microsystem technology
  - A master for the mold is made from a smooth thin layer of photosensitive polymer on a glass plate
  - The polymer is exposed to a laser beam that writes the data into the surface
  - The mold is then made by electroforming metal onto this polymer master
Microfabrication Processes

- Many MST products are based on silicon
- Reasons why silicon is a desirable material in MST:
  - Microdevices often include electronic circuits, so both the circuit and the device can be made on the same substrate
  - Silicon has good mechanical properties: high strength & elasticity, good hardness, and relatively low density
  - Techniques to process silicon are well-established

Differences between Microfabrication and IC Fabrication

Aspect ratio (height-to-width ratio) typical in (a) fabrication of integrated circuits and (b) microfabricated components
Examples

Cooling of Electronic Components

Liquid Chip Cooling for notebook computer

Research Project at Stanford Univ. Courtesy Alan Myers, Intel and Juan Santiago, Stanford

[Diagram showing liquid chip cooling system with labels for Heat Exchanger, Water Connector, and Electro-Osmotic Pump]
Formation of a thin membrane in a silicon substrate: (1) silicon substrate is doped with boron, (2) a thick layer of silicon is applied on top of the doped layer by epitaxial deposition, (3) both sides are thermally oxidized to form a SiO$_2$ resist on the surfaces, (4) the resist is patterned by lithography, and (5) anisotropic etching is used to remove the silicon except in the boron doped layer.

Surface micromachining to form a cantilever: (1) on the silicon substrate is formed a silicon dioxide layer, whose thickness will determine the gap size for the cantilevered member; (2) portions of the SiO$_2$ layer are etched using lithography; (3) a polysilicon layer is applied; (4) portions of the polysilicon layer are etched using lithography; and (5) the SiO$_2$ layer beneath the cantilevers is selectively etched.
LIGA Process

- An important technology of MST
- Developed in Germany in the early 1980s
- The letters LIGA stand for the German words
  - Lithographie (in particular X-ray lithography)
  - Galvanof ormung (translated electrodeposition or electroforming)
  - Abformtechnik (plastic molding)
- The letters also indicate the LIGA process sequence

LIGA processing steps: (1) thick layer of resist applied and X-ray exposure through mask, (2) exposed portions of resist removed, (3) electrodeposition to fill openings in resist, (4) resist stripped to provide (a) a mold or (b) a metal part
Urban-High Precision Machining

- Trends in conventional machining include taking smaller and smaller cut sizes
- Enabling technologies include:
  - Single-crystal diamond cutting tools
  - Position control systems with resolutions as fine as 0.01 μm
- Applications: computer hard discs, photocopier drums, mold inserts for compact disk reader heads, high-definition TV projection lenses, and VCR scanning heads

Example

- One application: milling of grooves in aluminum foil using a single-point diamond fly-cutter
  - The aluminum foil is 100 μm thick
  - The grooves are 85 μm wide and 70 μm deep
Ceramic Microchannels

Dimension (µm): 100

Dimension (µm): 50

Nanoparticles

Au Nanoparticles in Glass
Lycurgus Cup
Romans
4th century A.D.

Size in the range of 1-100 nm → Nanoparticles
**Nanoparticles**

- Au Nanowires
  - Kimura, 1995
  - *J. of Appl. Physics*

- C Nanotubes
  - *Wikipedia*

- ZnS Nanobelts
  - Yin, 2005
  - *Nature Materials*

- Pd Nanoclusters
  - Nathan, 2007
  - *Nanotech*

- Au Nanorods
  - Wu, 2005
  - *Chem. of Materials*

- Au Nanodots
  - Liu, 2002
  - *App. Physics Letters*

**Nanofabrication Processes**

- **Top-down approaches** – adaptation of microfabrication techniques to make nanoscale objects
- **Bottom-up approaches** – atoms and molecules are manipulated and combined to form larger nanoscale structures
Top-Down Approaches

- **Extreme ultraviolet lithography** – uses UV light with wavelength as short as 13 nm
- **Electron-beam lithography** – resolutions ~ 10 nm
- **X-ray lithography** - resolutions ~ 20 nm
- **Micro-imprint lithography** – uses flat mold with desired pattern that physically deforms resist surface to create regions that will be etched
- **Nano-imprint lithography** – same as micro-imprint but adapted to nanoscale

Micro-Imprint Lithography

(a) flat mold positioned above resist, (2) mold is pressed into resist surface, (3) mold is lifted, (4) remaining resist removed by etching to expose substrate surface.
Dip-Pen Nanolithography

Tip of an atomic force microscope is used to deposit molecules through the water meniscus that forms naturally between the tip and the substrate.

Bottom-Up Processing Approaches

- Production of materials
- Self-assembly
Self-Assembly

- A fundamental process in nature
  - Natural formation of a crystalline structure during slow cooling of molten minerals is an example of nonliving self-assembly
  - Growth of living organisms is an example of biological self-assembly
- In both instances, entities at the atomic and molecular level combine on their own into larger entities, proceeding in a constructive manner toward the creation of some deliberate thing

Self-Assembled Monolayers (SAMs)

- Two dimensional array (surface film) that is one molecule thick
- Molecules are organized in some orderly fashion
- Multi-layered structures also possible that are two or more molecules thick
Polymer Processing Lecture 7: Nanotechnology & Microfabrication

Research Focus

- **Polymer**
  - Cellulose with
    - John Simonsen
    - Sweda Noorani
    - Anand Mangalam
    - Valmika Nathan
    - Erik Sanchez

- **Metal**
  - Palladium with
    - Shalini Prasad
    - Valmika Nathan
    - Bhuvan Sekhar
    - Oksana Ostoverkhova
    - Vijay Mohanan

- **Ceramic**
  - Silicon Nitride with
    - Sho Kimura
    - Kartavya Jain
    - Goran Jovanovic
    - Vinod Narayanan
    - Sukumar Roy
    - Vince Sprekle

Metal Nanoparticles

- Palladium in Polycarbonate
  - Valmika Nathan

- Gold in Polystyrene_b_Ethylene Oxide
Synthesis of Pd Nanoclusters

- Metal salt: PdCl₂
- Organic ligand: Dodecanethiol or Polycarbonate
- Reducing agent: NaBH₄

Brust Method

Synthesis of Pd Nanocomposites

- Brust Method
  - ex situ synthesis
    - Pre-synthesized Pd nanoclusters + PC matrix
  - in situ synthesis
    - Reduction of PdCl₂ in the presence of PC

Film casting
Morphological Changes

- **ex situ** Pd/PC nanocomposites: discrete nanoclusters
- **in situ** Pd/PC nanocomposites: agglomerated nanoclusters

Valmika Nathan

Possible Mechanisms

• **in situ**: rate of clustering > rate of capping by PC, higher molecular weight of PC.

**Electrical Properties**

*in situ* samples are semi-conducting in nature

**Possible Reason:** Agglomerated

(Rao, 2006, *Catalysis Communications*)

Valmika Nathan

---

**Application: Sensors**

Diwakara Meka
Shalini Prasad
Chemical Sensors

Polymer- Pd/Polycarbonate Nanocomposite

NO$_x$ detection

Valmika Nathan
Diwakara Meka
Shalini Prasad

Polymer Nanoparticles

Cellulose Nanocrystals (CNXLS)
Source: Simonsen, 2004

Turnip Yellow Mosaic Virus Capsids (TYMV)
Source: Michels et al, 1999
**TYMV Capsids**

- 28 nm O.D. and 26 nm I.D.
- 7 nm pore formed during freeze-thaw
- 180 copies of a single 20K MW protein
- self-assembled surface arrays
- cavity sensors, controlled drug release

**CNXLs**

Cellulose Nanocrystals in Natural Microsystems
Oksman & Sen, 2006
*Cellulose Nanocomposites*
Synthesis of CNXLs

Native cellulose
Crystalline domain
Amorphous domain

Acid hydrolysis

Individual nanocrystals

Polysulfone/CNXL Nanocomposites

0 % CNXL
2 % CNXL
11 % CNXL
16 % CNXL

Sweda Noorani & John Simonsen
Permeability: Water Vapor

![Graph showing permeability of water vapor vs. % Cellulose nanocrystals]

Sweda Noorani & John Simonsen

Kidney Dialysis Membranes

CNXL composite membranes for improved selectivity and stiffness

Urval, 2004

Micro Channel-Based Dialyzers
Goran Jovanovic & John Simonsen
Ceramic Nanoparticles

Silicon Nitride
(Si₃N₄)
Kimura, 2003

Silicon Carbide
(SiC)
Bothara et al, 2007

Ceramic Nanoparticles: SiC

Plasma Pressure Compaction

Microstructure

Work

Process Model

Armor

Electronic Packages

Manish Bothara
Future Outlook: Process Integration

Safety: limits environmental exposure
Other processes: mixing, molding & extrusion

Bottom-line: safer nanotechnology

HW 5

None
You should have learnt …

- Microsystems Technology
- Microfabrication and Nanofabrication Processes
- Applications
- Research Issues

Next Class

- Other Polymer Processes (Chapters 7 & 8)