Soft Lithography and Materials Properties in MEMS

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*** With thanks to Steve Senturia and Joel Voldman, from whose lecture notes some of these materials are adapted.**

Outline

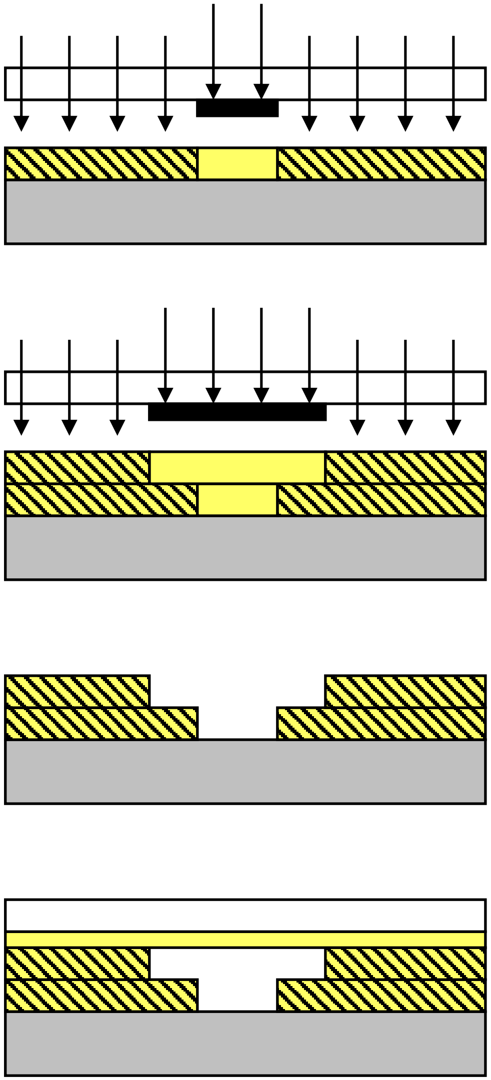
> **Soft Lithography**
- **Materials and processes**
- **Patterning biomaterials**

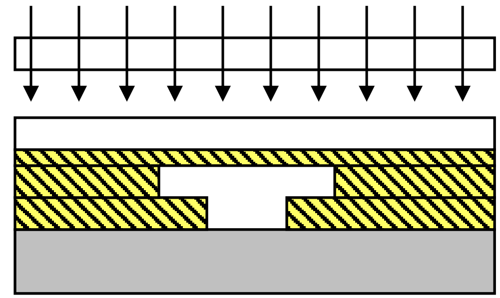
> **Material Properties in MEMS**
- **Role of material properties in MEMS**
- **Some examples**
- **Determining material properties**

SU-8 Epoxy

- Near-UV photosensitive epoxy that acts as a negative resist
- High aspect ratio structures possible (20:1), up to mm
- BUT it is not readily removed like photoresist would be
- Can be a structural material or a mask/mold for other materials
- Multilayer processing for thicker structures or two layer structures, including enclosed flow paths
- Hydrophobic (adheres best to hydrophobic materials)
- Challenges:
  - Mechanical stress, cracking
  - When used as a mask, difficult to remove

Sample process: multilayer SU-8 microfluidics





> Spin coat, prebake, expose, and postbake first layer

> Spin coat, prebake, expose, and postbake second layer

> Develop both layers

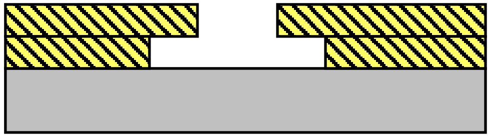
> Cap with SU-8 coated transparent plate

> Expose to crosslink SU-8 “glue”, final bake

Described in Jackman, J. Micromech. & Microeng. 11, 2001, 263.

Multilayer SU-8 options

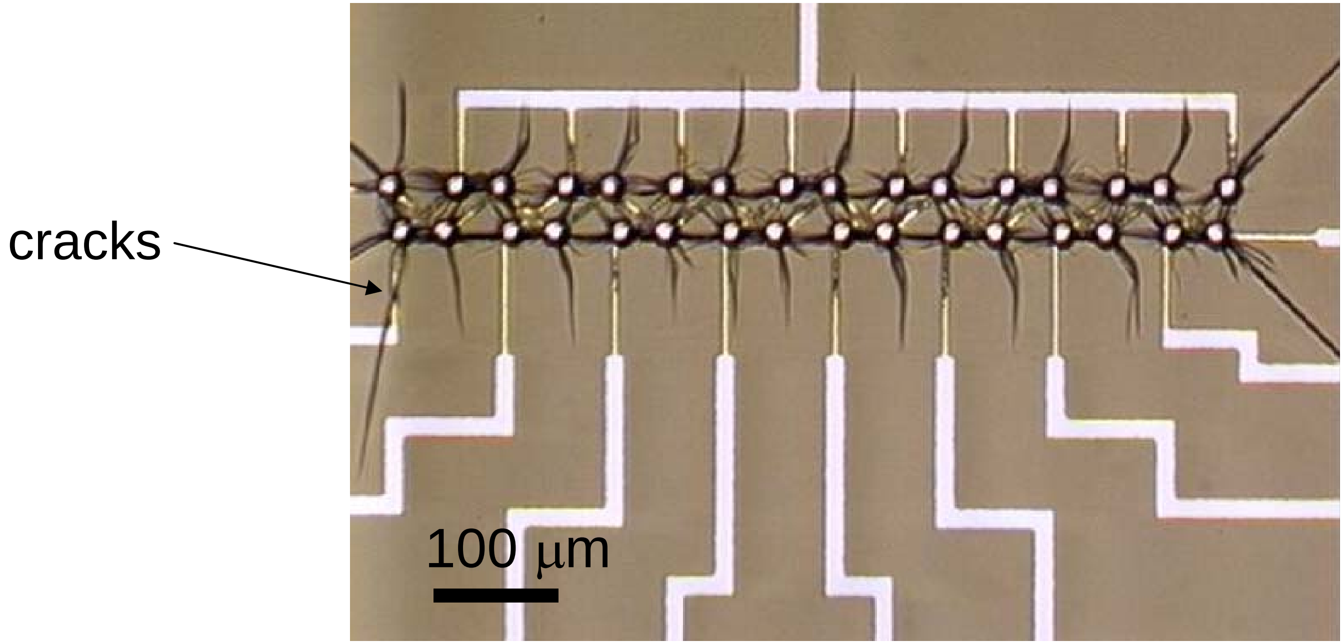
- **Challenge: suspended structures**
  - **Unintended exposure of first layer can destroy undercut**



- **Some demonstrated options:**
  - **Deposit metal on top of undeveloped first layer to protect it from second exposure**
  - **Develop first layer channels and fill with a sacrificial polymer to be removed later**
  - **Expose only the upper layer of SU-8 by controlling dose and/or focal depth**

Cracking in SU-8

- **SU-8 shrinks in developer, causing cracks and loss of adhesion**



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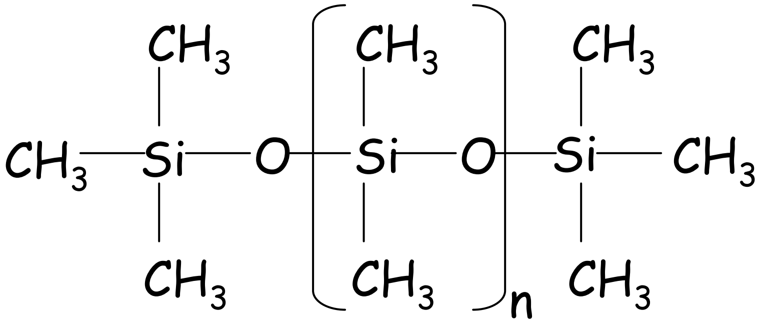
SU-8 Removal

- When using SU-8 as a resist and not a structural material, it must be removed!
  - Enduring challenge – best option is not to strip the SU-8
- Postbaked material extremely chemically resistant
  - Wet
    - Piranha, also removes other materials
    - Nanostrip, but much slower
    - Organic SU-8 removers
      - Work by swelling and peeling, not dissolution
  - Dry
    - O_2 plasma for "cleanup", too slow for bulk removal
  - Sacrificial layer: "Omnicoat"
    - Organic layer, O_2 plasma patternable
    - Spin-coat sacrificial layer, process SU-8 on top
    - Sacrificial layer permits SU-8 "liftoff"

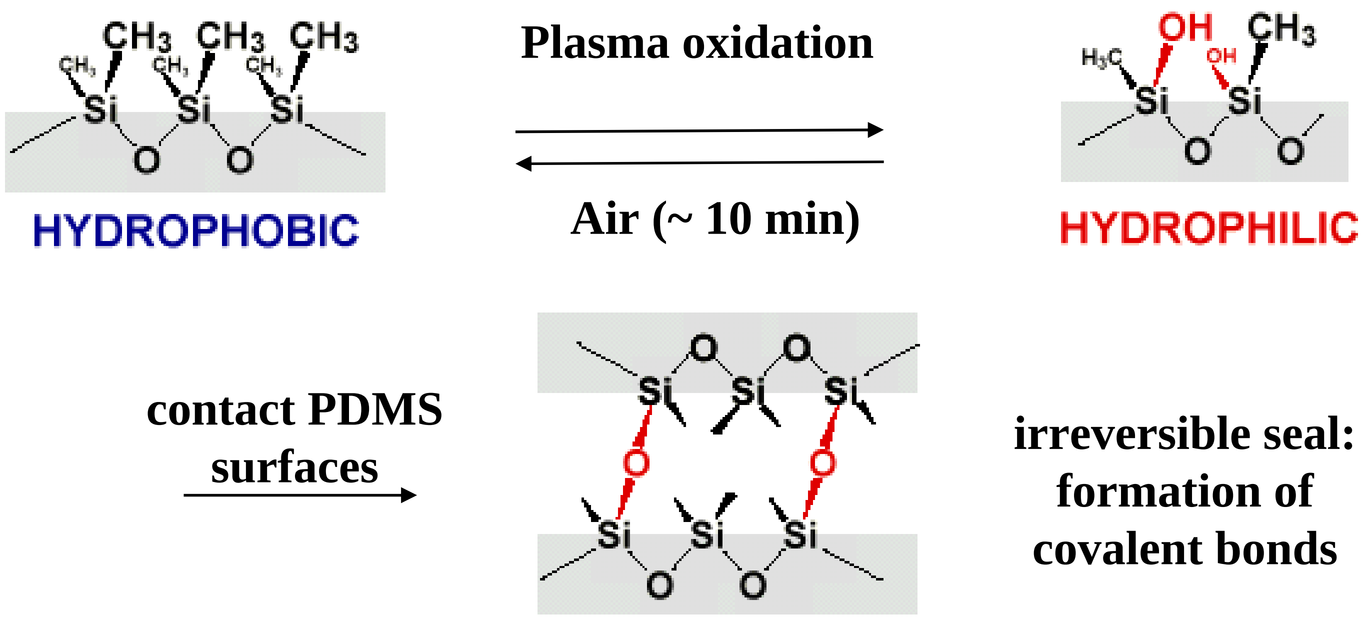
PDMS

- Polydimethylsiloxane
- Flexible elastomer
- Used to replicate topography from a master (Si, SU-8, etc)
- Used as a conformable stamp for patterning onto other surfaces
- Good for sealing microfluidic devices; can be sealed to many materials
- Can be spin-coated
- Possible to dry etch
- Low cost pattern replication

PDMS

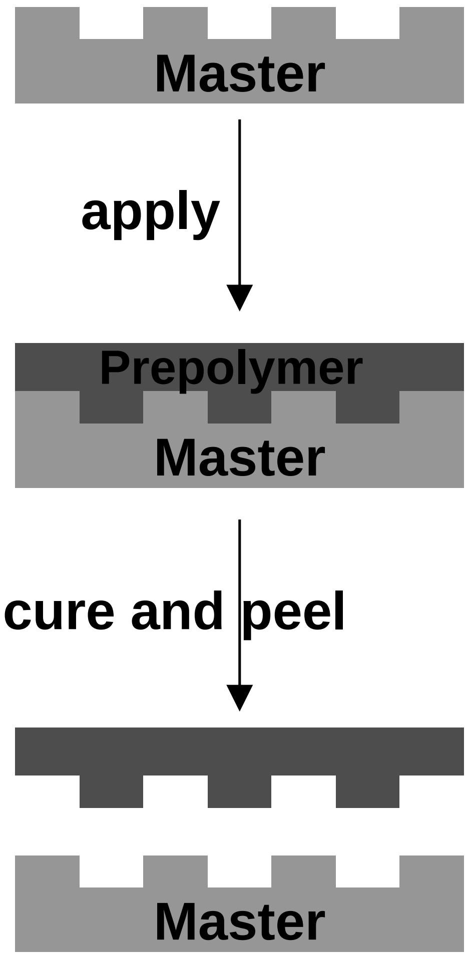


> Upon treatment in oxygen plasma, PDMS seals to itself, glass, silicon, silicon nitride, and some plastic materials.



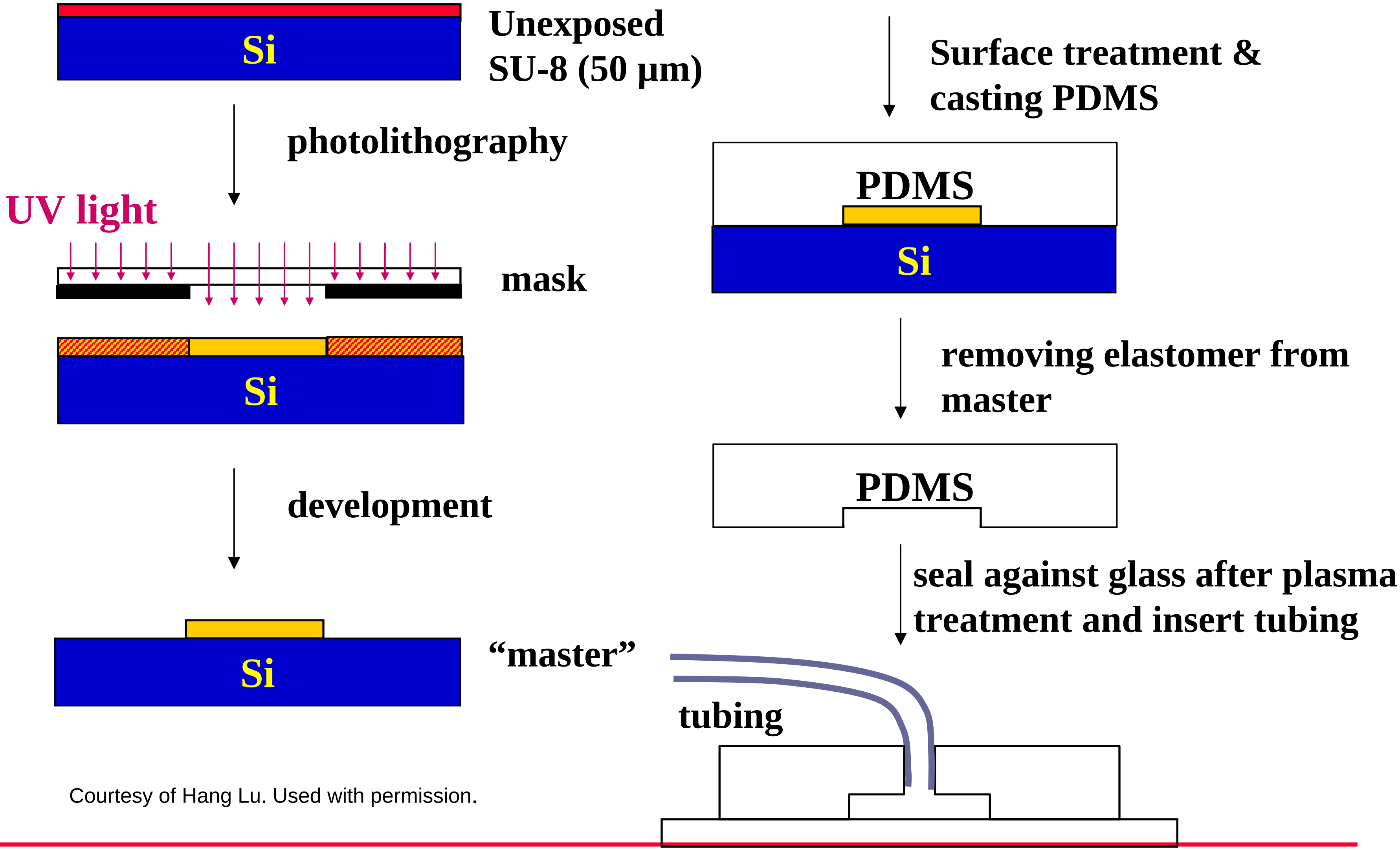
Courtesy of Hang Lu and Rebecca Jackman. Used with permission.

Pattern replication by molding



- Master can be silicon, SU-8, photoresist, or elastomer
- Apply prepolymer liquid to master
- Cure (by baking) and peel off
- When molding with PDMS, can exploit PDMS sealing to form enclosed microchannels

Sample PDMS Process



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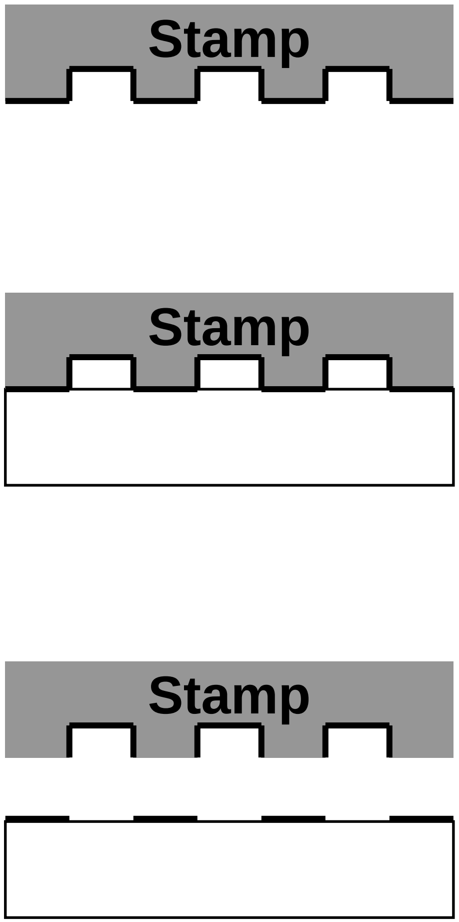
Microcontact printing



- **Apply ink to an elastomer stamp**
- **Bring stamp in contact with surface (need not be flat because stamp can deform)**
- **Ink transfers to surface of substrate**
- **Can be used to mask etches, depositions, etc**
- **Inks:**
  - **SAMs (alkanethiols for coating on noble metals), organics, proteins, etc.**
- **Size scale: submicron to millimeters**

Microcontact printing on non-planar surfaces

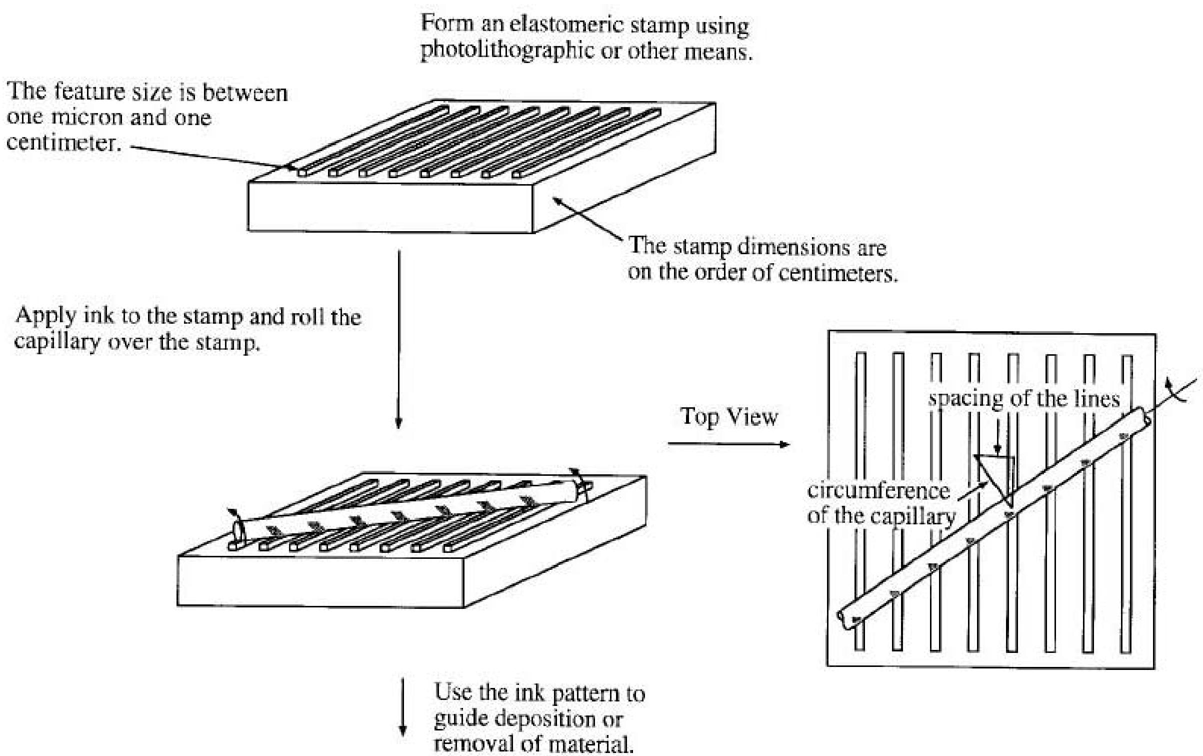
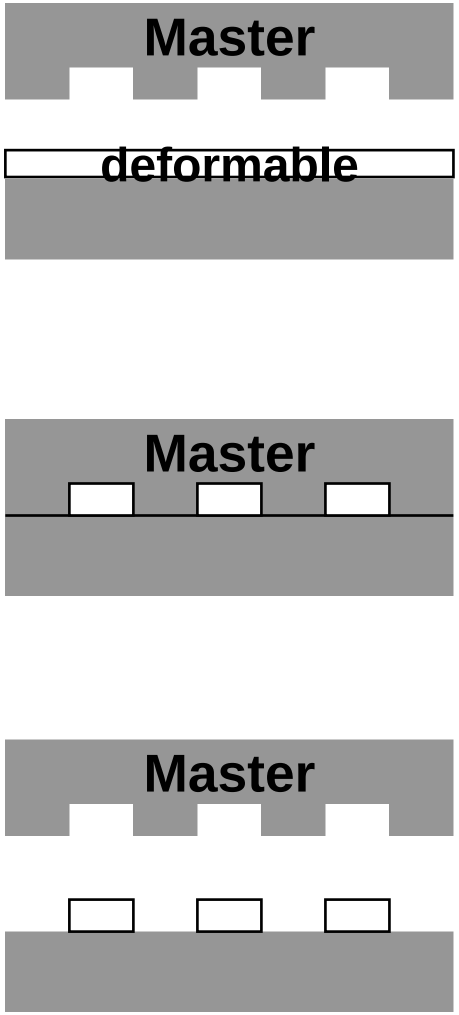


Figure 2 on p. 186 in Rogers, J. A., R. J. Jackman, and G. M. Whitesides. "Constructing Single- and Multiple-helical Microcoils and Characterizing Their Performance as Components of Microinductors and Microelectromagnets." *Journal of Microelectromechanical Systems* 6, no. 3 (Sept. 1997): 184-192.

Pattern replication by imprinting



- Imprint in a thermoplastic material by heating and applying pressure
- Typical material: PMMA (polymethyl-methacrylate)
- Or imprint in UV-curable fluid, like polyurethane
- Process usually leaves trace material in “clear” areas, which may be removed by dry etch
- Can replicate nanoscale features (nanoimprinting, S. Chou)

Parylene

- A vapor-deposited polymer that provides very conformal coatings
- Thickness range: submicron to about 75 microns
- Chemically resistant, relatively inpermeable
  - Component encapsulation
- Low friction film can act as a dry lubricant
- Low-defect dielectric insulating layer
- Relatively biologically inert
- Thin films nearly transparent
- Low stress – minimizes interaction with components
- Can be dry etched

Some other useful materials

- Polyurethane
  - UV-curable is particularly useful, can be used for molding process
- Special purpose polymers (not all terribly mainstream, but an active and useful area of development):
  - Photodefinable polycarbonate that decomposes at 250C (ie Unity Sacrificial Polymer)
  - Avatrel, a polymer material through which decomposed Unity can diffuse

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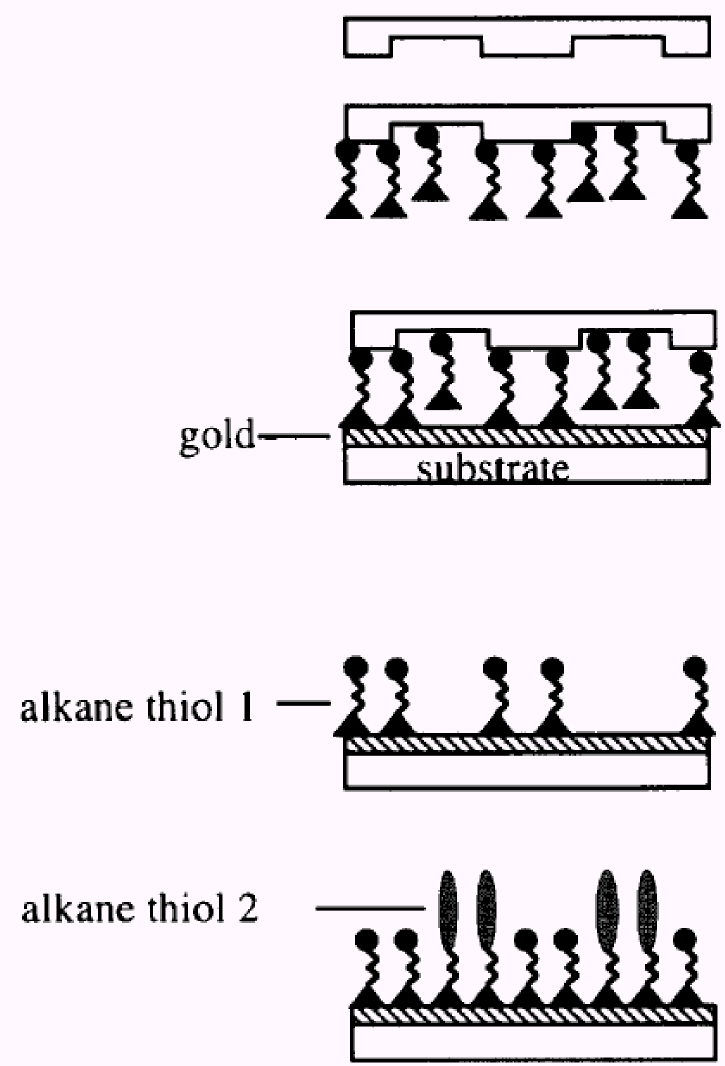
Biomaterials processing

> **Biomolecules – DNA, proteins, cells**

- **Needed for biosensors, cell arrays, etc.**
- **Challenge is integrating fragile molecules with semiconductor processing**
- **Multiple methods**
  - » **Micro-contact printing**
  - » **Microfluidic patterning**
  - » **Lift-off**
  - » **Stencils**

Biomaterials processing by microcontact printing

> **Microcontact printing**
  - **Developed by Whitesides at Harvard Univ.**
    - » **Xia & Whitesides, Annu. Rev. Mater. Sci. 28:153, 1998.**
  - **No harsh solvents needed**

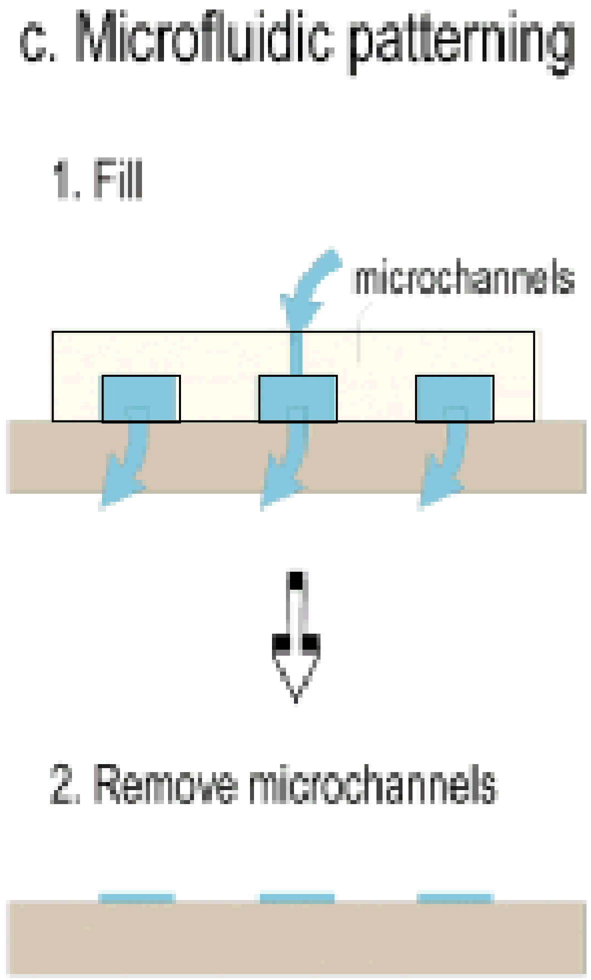


Courtesy of Elsevier, Inc., http://www.sciencedirect.com. Used with permission.
Figure 4 on p. 601 in: Blawas, A. S., and W. M. Reichert. "Protein Patterning."
Biomaterials 19, nos. 7-9 (April 1998): 595-609.

Biomaterials processing by microfluidic patterning

> Microfluidic patterning

- Attach PDMS stamp to substrate
- Add biomolecule to solution
- Flow solution through channels
- Attachment via adsorption



Courtesy of Annual Reviews. Used with permission.
Figure 1c) on p. 230: in Folch, A., and M. Toner. "Microengineering of Cellular Interactions." *Annual Review of Biomedical Engineering* 2 (August 2000): 227-256.

Biomaterials processing by liftoff

> **Lift-off**
> - **Use standard photoresist lift-off**
> - **Molecules must withstand acetone or other solvent**

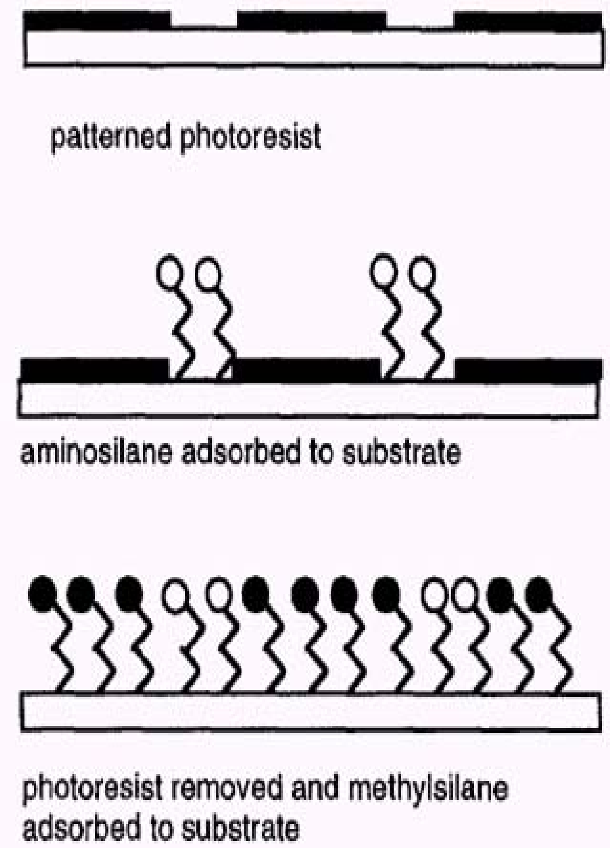


Figure 1 on p. 597 in: Blawas, A. S., and W. M. Reichert. "Protein Patterning.“ *Biomaterials* 19, nos. 7-9 (April 1998): 595-609.

Biomaterials processing by stencils

> Stencils

- **Use PDMS stamps as dry resists**
- **Physically pattern biomaterials**
- **Can use with most any substrate**
- **Potential damage to cells on feature periphery**

Image removed due to copyright restrictions.
Figure 3 on p. 351 in: Folch, A., B. -H. Jo, O. Hurtado, D. J. Beebe, M. Toner. "Microfabricated Elastomeric Stencils for Micropatterning Cell Cultures." *Journal of Biomedical Materials Research* 52, no. 2 (2000): 346-353.

PDMS stencil
A Folch, Univ. Washington

a) Attach stencil to substrate
b) Add cells
c) Let cells attach to substrate
d) Remove stencil

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Material properties and coupled domains

> The basic functionality of many MEMS devices is in coupling one domain to another, and this coupling is typically described by material properties
  - Mechanical to electrical
  - Electrical to thermal
  - Thermal to fluids

> The failure modes of many MEMS devices are in coupling one domain to another
  - For example, package stress interacting with piezoresistor

> Some properties of MEMS materials are exceptional
  - Pronounced piezoresistivity of silicon

“Off-label” use of materials

- MEMS devices often depend on material properties that are less important for other uses of the material
- Fracture strength of Si
- Biocompatibility of Si-based materials

Process dependence

- Some microelectronic materials, like single crystal silicon, have highly predictable and repeatable constitutive properties
- Most microelectronic materials, however, exhibit some degree of process dependence in their material properties, especially deposited or thermally formed thin films
- Some properties, like thin-film residual stress, can be wildly dependent on deposition conditions, even changing sign from compressive to tensile

Planning around material properties

> **Well-controlled material properties can pose a design challenge**
  - **Many factors, may point design in opposite directions**

> **Poorly-controlled material properties are worse**
  - **Every device has specifications, which must be met by either getting it right the first time or employing some combination of trim (fixing the hardware later) and calibration (compensating through software)**
  - **“Getting it right” includes both materials and geometry**
  - **The greater the variation in properties, the greater the headache and the greater the cost**

Constitutive Properties

- **Constitutive properties are normally expressed as relationships between applied loads ("causes") and resulting responses ("effects").**
- **It is not always clear which is which. If the functional relation can be inverted, it doesn't actually matter.**

Examples of constitutive properties

Load	Response	Property
Distributed mechanical force	Acceleration	Mass density
Temperature rise	Increase in internal energy per unit volume	Specific heat per unit volume
E-field	D-field	Dielectric permittivity
H-field	B-field	Magnetic permeability
Stress	Strain	Elastic compliance
E-field	Current density	Electrical conductivity
Temperature gradient	Heat flux	Thermal conductivity
Shear stress	Shear rate	Inverse of viscosity

Scalar properties

> **Scalar properties are those which involve no orientation-dependent or direction-dependent effects**

> **Examples:**
- **Mass density**
- **Specific heat**
- **Viscosity of a gas or unoriented liquid (i. e. not a liquid crystal)**
- **And, for isotropic materials: permittivity, permeability, electrical and thermal conductivity**

Tensor properties

- Properties that involve directions, either the relative directions of applied vector loads and vector responses, or the orientation of loads and/or responses relative to internal (crystalline) axes, require tensors for their specification
- Examples:
  - Permittivity, permeability, index of refraction and conductivity of non-cubic solids are second-rank tensors
  - Piezoelectric responses which couple stress and strain to electric fields are described with third-rank tensors
  - Elastic constants and piezoresistive responses require fourth-rank tensors
- Because constitutive properties have lots of symmetry, we can usually boil these higher-order tensors down to something manageable.

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Which properties to consider?

- One of the challenges for the MEMS designer is knowing what you should care about.
- One course goal is acquiring domain knowledge, which gives you some insight into which material properties are important in a given situation.
- Today: a sneak preview of what you might worry about
- A useful resource:
  - A previous year's assignment involved looking up material properties for many MEMS materials.
  - Results are posted on the web site.
  - Buyer beware! This is the work of 20 + students and surely contains some errors.

Electrical Conductivity

- Relates electric field to current density; Ohm's law minus the geometry.
- Importance: circuits, sensors
- Elemental metals: observed values can vary from tabulated bulk values, depending on deposition method.
  - Example: a factor of two variation in metals printed as nanoparticles in a solvent and then annealed.*
- Other materials: variations much more pronounced
  - Polysilicon conductivity depends on grain size, doping: orders of magnitude with relatively small process variations.
- Characterize by four-point measurement of test structures with known geometry.

** Fuller et al, JMEMS, vol. 11, p. 54 (2002).*

Breakdown Strength

- The maximum electric field that an insulating material in the gap between two flat electrodes can withstand without suffering dielectric breakdown
- Depends on the size of the interelectrode gap
- Importance: high voltage actuators, maximum performance
- Can vary with film composition, defect density
- Tabulated values are sufficient if the design does not push the limits; otherwise characterization is necessary.
- One test approach: fabricate a capacitor and fill gap with material in question. Match gap thickness to actual device. Detect onset of breakdown both optically and by current flow.

Elastic constants

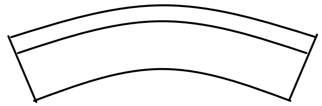
- Relate stress (how hard you push or pull on something in a given direction, per unit area) to strain (the resulting fractional change in the object's length or shape)
- Importance: how far will your cantilever or membrane deflect?
- Single crystal materials: good reproducibility
- Deposited materials: must be characterized
- Characterizing elastic constants in MEMS is a significant challenge. Stay tuned for some sample approaches at the end.

Residual film stress

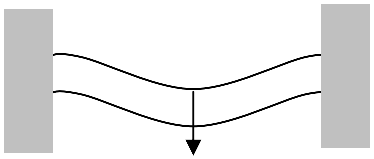
- Stress in a film deposited on a Si wafer, in the absence of external loading.
- Two flavors:
  - Intrinsic stress: related to structure
  - Thermal stress: accumulated from a change in temperature
- Residual stress is a VERY VARIABLE PROPERTY, and must be measured.
- Can play games, such as adjusting deposition conditions to ensure that intrinsic and thermal stresses cancel out at given T
- One basic characterization: wafer curvature in the presence of a blanket film
- More advanced approaches later in lecture

Known problems from residual stress

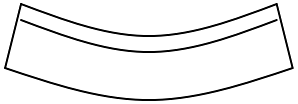
- Deformation of free, moveable structures
  - Compressive film on a wafer
    - Wafer bows



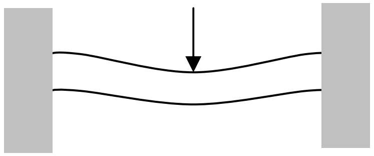
  - Compressive membrane or beam
    - Buckling
    - Operational deflection can be enhanced



  - Tensile film on a wafer
    - Wafer bows



  - Tensile membrane or beam
    - Operational deflection can be reduced



- Film cracking and delamination

Coefficient of Thermal Expansion (CTE)

- Fractional change in length per unit temperature change
- Importance: CTE mismatch plus high T processing or operation creates stress (and deformation and/or destruction)
- Examples:
  - Bonding glass (quartz or Pyrex) to Si
  - Thermal stress in a film that is deposited at high T
- CTE is tabulated, and one of the less variable material properties.

Piezoresistance

> Straining the silicon lattice shifts the band-edge energies of the conduction band and the valence band
  - The conduction band, in particular, consists of multiple minima and, depending on the direction of the strain, some go up more than others
  - This shifts the relative electron population in some minima compared to others and modifies scattering rates

> Result: an orientation-dependent shift in the conductivity

> For historical reasons, the piezoresistive coefficients relate resistivity to stress.

> Piezoresistivity is good for strain sensors, and sometimes changes the resistance of otherwise perfectly good resistors.

> Coefficients are material, orientation, temperature, and doping dependent

Analytic Formulation of Piezoresistance

- The electric field E is a vector (first-rank tensor)
- The current density J is a vector (first-rank tensor)
- Therefore, the resistivity ρ_e (and/or conductivity) is a second-rank tensor, as is the stress σ
- The piezoresistive effect is described by a fourth-rank tensor

$$\mathrm{E} = \left[\rho_e + \Pi \cdot \sigma\right] \cdot J$$

The Details

- **Good news: in cubic materials, there are just three independent non-zero piezoresistance coefficients, π_{11}, π_{12}, π_{44}.**

Effect of stress along direction of E

Effect of stress perpendicular to E

Ohm's law

Effect of shear stress

$$\frac{\mathrm{E}_1}{\rho_e} = \left[1 + \pi_{11}\sigma_1 + \pi_{12}(\sigma_2 + \sigma_3)\right]J_1 + \pi_{44}\left(\tau_{12}J_2 + \tau_{13}J_3\right)$$

$$\frac{\mathrm{E}_2}{\rho_e} = \left[1 + \pi_{11}\sigma_2 + \pi_{12}(\sigma_1 + \sigma_3)\right]J_2 + \pi_{44}\left(\tau_{12}J_1 + \tau_{23}J_3\right)$$

$$\frac{\mathrm{E}_3}{\rho_e} = \left[1 + \pi_{11}\sigma_3 + \pi_{12}(\sigma_2 + \sigma_1)\right]J_3 + \pi_{44}\left(\tau_{13}J_1 + \tau_{23}J_2\right)$$

where

$$\rho_{\mathrm{e}}\pi_{11} = \Pi_{1111}, \ \rho_{\mathrm{e}}\pi_{12} = \Pi_{1122}, \ \rho_{\mathrm{e}}\pi_{44} = 2\Pi_{2323}$$

Piezoresistivity in Silicon

- **Coefficients depend on doping, and decrease rapidly above about 10^{19} cm^{-3}**
- **Coefficients are functions of temperature**
- **Typical values**

Type	Resistivity	$\pi 11$	$\pi 12$	$\pi 44$
Units	Ω-cm	10^{-11} Pa^{-1}	10^{-11} Pa^{-1}	10^{-11} Pa^{-1}
n-type	11.7	-102.2	53.4	-13.6
p-type	7.8	6.6	-1.1	138.1

Piezoelectricity

> **Ionic crystals that lack a center of inversion symmetry can exhibit a net polarization within each unit cell. Materials which have this at zero strain are called ferroelectrics. Materials in which the dipole results from strain are called piezoelectrics**

> **Examples**

- **Quartz**
- **Zinc oxide**
- **Lithium niobate**
- **Lead zirconate-titanate (PZT)**
- **Aluminum nitride**
- **poly (vinylidene fluoride)**

Piezoelectricity

- Piezoelectrics can have a net electric polarization which interacts with mechanical strain
  - Applying a voltage across a piezoelectric creates strains both parallel and perpendicular to the applied electric field (actuation)
  - Straining a piezoelectric creates an electric field both parallel and perpendicular to the imposed strain (sensing)
- Interaction between stored mechanical energy and stored electrostatic energy
  - Permits both sensing and actuation
  - Unlike piezoresistivity, which is purely dissipative (no actuation)

Piezoelectric coefficients

- The piezoelectric tensor links the stress tensor to the electric polarization tensor
- There are four variables: stress, strain, electric field, and electric displacement
- Simplification by symmetry: the behavior can be captured by either the “d coefficients” (when stress and electric field are the independent variables) or by the “e coefficients” (when strain and electric field are the independent variables)
- The d coefficients (units C/N) relate strain to electric field
  - Consider an electric field in the z direction
  - Strain in the x or y direction = d_{31}*Electric field in the z direction
  - Strain in the z direction = d_{33}*Electric field in the z direction

Piezoelectric materials

> **Some piezoelectrics have no net polarization at zero strain**
- **Quartz**
- **Zinc oxide**
- **Quartz and ZnO are stiff materials, with low strain**

> **Some materials have a net polarization at zero strain**
- **Common example: PZT (Lead zirconate titanate)**
- **Higher strain ceramic material for larger deflections**
- **Common choice for MEMS devices**
- **Fabrication: deposited in layers by a sol-gel (spin on) process, thermally cured, then poled in an electric field**

> **Piezoelectric polymers**
- **Example: poly (vinylidene fluoride)**
- **Very high strains**

Examples of piezoelectric coefficients

> **Zinc oxide**

- **d_{31} = - 5.4 pC/N**
- **d_{33} = 11.7 pC/N**
- **Note: expansion along the field corresponds to contraction in the transverse direction**

> **PZT**

- **Coefficients depend on exact PZT material, on underlying material, on frequency, and on electric field**
- **- d_{31} is in the ballpark of 100 pC/N to several hundred pC/N**
- **d_{33} is in the ballpark of several hundred pC/N to 1000 pC/N**
- **Again, expansion along the field corresponds to contraction in the transverse direction**

Variation over temperature

- Electrical conductivity
- Thermal conductivity
- Specific heat
- Coefficient of thermal expansion (CTE)
  - Variations in the coefficient itself
- Piezoresistive coefficients
- Piezoelectric response (pyroelectricity)
- Young's modulus

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The bottom line

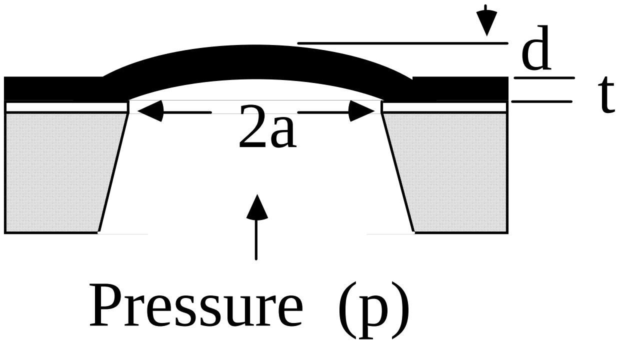
- You need to use test structures to characterize materials with variable properties
- Measuring electrical properties requires electrical test devices
- Measuring mechanical properties requires a mechanical test device
  - Basically a MEMS device designed to help you measure a particular property value or values
  - Fabrication of test device must accurately reflect fabrication processes that you will use to create your real device
- Measuring material properties requires as much careful design and fabrication as is required to create a device

What’s Hard?

- Knowing the geometry of the test device well enough to be able to make good measurements of the constitutive properties and their repeatability
  - Lateral and vertical dimensions not too difficult
  - Sidewall angles, mask undercut are harder
- Modeling the test device accurately enough so that the accuracy of the extracted properties are limited by geometric errors
  - A good procedure is to make a family of test structures with a systematic variation in geometry, and extract constitutive properties from all of the data.
- Preventing systematic errors in the measurement

Membrane Load-Deflection Example

- The problem: residual stress and stiffness of membranes affect their deflection under load
- Example: pressure sensors



- Approach:
  - Apply different pressures and measure resulting deflections
  - Fit to an energy-based model for large membrane deflections
  - Ideal rigid boundary conditions are a benefit
- Weakness:
  - Deflection is very sensitive to variations in membrane thickness and edge length, so metrology errors appear
  - How to get a family of test geometries?

Pull-in of beams: M-Test Example

- **The problem: elastic constants and residual stress affect the actuation of mechanical MEMS structures**
- **Approach:**
  - **Fabricate an array of microbeams of different lengths**
  - **Measure the voltage at which they “pull in”, and fit to models**
  - **Excellent agreement with known values when boundary conditions are ideal**

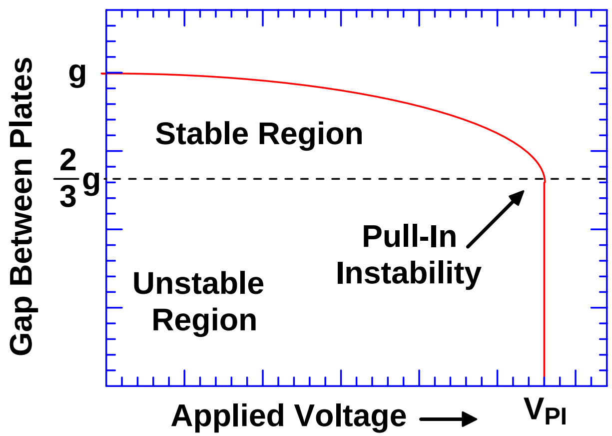


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Figure 10 on page 116 in: Osterberg, P. M., and S. D. Senturia. "M-TEST: A Test Chip for MEMS Material Property Measurement Using Electrostatically Actuated Test Structures." *Journal of Microelectromechanical Systems* 6, no. 2 (1997): 107-118.

- **Weakness: surface micromachined beams often have some support compliance**