NACK NETWORK

Building College-University Partnerships for Nanotechnology Workforce Development

PDMS: An Example of a Versatile Material for Micro- and Nanotechnology

Outline

- Background
- Properties of PDMS
- Applications of PDMS
- Modification of PDMS

Background

PDMS is Polydimethylsiloxane

Polysiloxane discovered by Dow Chemical

Good elastomer / flexibility

```
   R   R                      R    R
    \ /                ↔       \  /
—O—Si—O —                       Si
                               /  \
                            — O    O—
```

Figure 1: The above representation of the PDMS molecule shows the flexibility of the entire backbone chain.

Background

There are at least six forms of commercially viable PDMS products that are common:

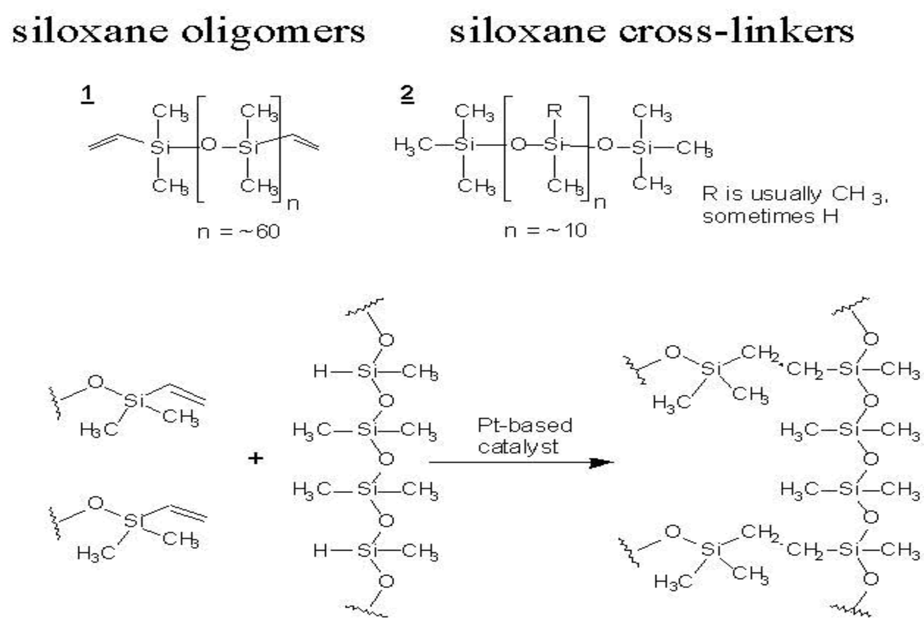
- Fluids
- Emulsions
- Compounds
- Lubricants
- Resins
- Elastomers or rubbers

Background

- As shown in the last slide PDMS has many forms and uses. It is especially useful because it is relatively inexpensive.
- Our focus will be on PDMS as a "substrate". It is especially useful for microfluidics.
- Another very good example of a PDMS application is soft contact lens.
  – The lenses are inexpensive, have exacting tolerances, and must be biocompatible.

Background

<u>Chemical Structure</u>: A no waste reaction



The bonding of the siloxane oligomer and cross-linkers along with the catalyst reaction. (Oligomer is a polymer or polymer intermediate that has relatively few structural units)

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Properties of PDMS

- Its unique surface properties such as low surface tension are ideal for : Paper release agents, fiber lubricants, textile hand modifiers, mold release agents, anti-fouling materials and water repellents.
- It is transparent, pliant, biocompatible, permeable to oxygen, chemically inert, homogeneous, and has low water absorption. Hydrophobicity can be altered to suit the application.
- Resistant to sunlight, moisture, heat, cold, aging, or weather.

Properties of PDMS

The ratio of base to curing agent, is a 2 part mixture: 1:1 or 10:1

Room temperature curing may take a full day, or fast curing is accomplished using heat.

Safety Issues: Benign

National Fire Protection Agency (NFPA) rating:

Cure - Health -**0** Flammability – **0** Instability/reactivity – **1**

Base – Health – **0** Flammability – **1** Instability/reactivity – **0**

Overexposure risk is minimal

PDMS Form Sylgard-184

- Mixture of the curing agent and the base components in a 10:1 ratio (by weight).
- De-gas the mixture by vacuum to draw air to the surface.
- Curing for 24 hours at 23°C; 4 hours at 65°C; 1 hour at 100°C; or 15 minutes at 150°C.

Cost of PDMS

Cost of PDMS – Pricing of a ½ Kilo of PDMS (approx. 1.1lbs.) $40.00

Equipment – Spinner @ $6k – 8k

Squeegee or similar device

under $10.00

Hot Plate for under $500

PDMS has a shelf life of 24 months for an unopened container from the date of manufacture.

Suppliers of PDMS

- Sigma-Aldrich - Poly(dimethylsiloxane)
- Dow Corning - Sylgard 184
- Polysciences Inc. - Poly(dimethylsiloxane)

Product Comparison

Cost Comparison for PDMS				
CAS Number	**Brand Name**	**Manufacture**	**Quantity**	**Cost**
70131-67-8	Polydimethylsiloxane	Alfa Aesar	6.6 Gal	$260
NA	Sylgard 184	Fisher Scientific	1.1 Gal	$52
NA	TRANS-30 (PDMS)	Trans-Chemco	1.1 Gal	$47

Product Comparison

Cost Comparison for PDMS				
CAS Number	**Brand Name**	**Manufacture**	**Quantity**	**Cost**
63148-62-9	Poly(dimethylsiloxane)	Sigma-Aldrich	1 L	$120
68037-59-2	Sylgard 184	Dow Corning	1.1 lb	$40
63148-62-9	Poly(dimethylsiloxane)	Polysciences Inc.	250g	$116

Product Comparison

Manufacture	Quantity	Density	Viscosity	Form	Cost
Alfa Aesar	1.1 Gal	0.97 g/mL	105 mPa.sec	Liquid	$43
Fisher Scientific	1.1 Gal	1.33 g/mL	4000 mPa.sec	Liquid	$52
Trans-Chemco	1.1 Gal	1.02g/mL	3500 mPa.sec	Liquid	$47

Product Comparison

Manufacture	Quantity	Density	Viscosity	Form	Cost
Sigma-Aldrich	1 L	0.97 g/mL	100 mPa.sec	Liquid	$181
Dow Corning	1.1 lb	1.03 g/mL	3900 mPa.sec	Solid	$40
Polysciences Inc.	250g	1.02 g/mL	80 mPa.sec	Solid	$116

Outline

- Background
- Properties of PDMS
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Applications of PDMS

- PDMS Stamp Fabrication Methods
- Various Soft Lithography Techniques
- Microfluidic Channel Casting
- Implanted Biomedical Microsystems

PDMS Stamps Using SU-8 Resist

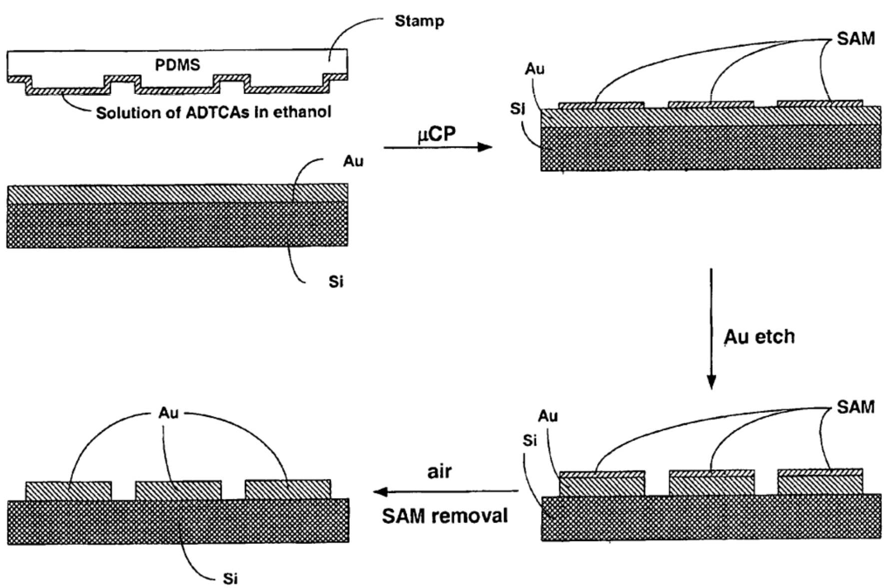
- Commonly used to fabricate polymeric microfluidic structures.
- SU-8 has high a viscosity, and the ability to define layers between 1 and 200µm with high aspect ratio and vertical sidewalls.
- SU-8 is patterned with contact lithography. The PDMS mixture is added on the SU-8 master, cured, and then, peeled off.

Soft Lithography

- Use of elastomeric stamps or molds to transfer patterns onto a surface with different techniques:
  - Microcontact printing (μCP)
  - Replica Molding (REM)
  - Microtransfer Molding (μTM)
  - Micromolding in Capillaries (MIMIC)
  - Solvent-assisted Micromolding (SAMIM)
  - High Aspect Ratio Microstructure Replication (HARM)

Microcontact Printing (µCP)

- Generates micropatterns of self-assembled monolayer (SAMs) .
- Transfer of the “ink” molecules from the PDMS stamp to the substrate by contact.
- The use of PDMS stamps for µCP, make the patterning of nonplanar surfaces possible.
- Features as small as 300nm

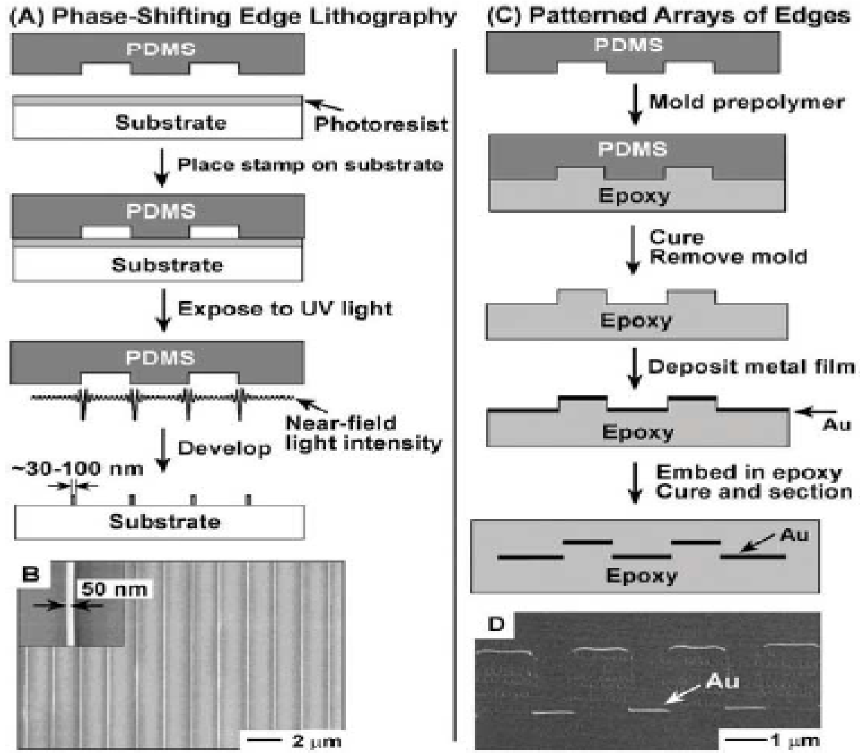


United States Patent 6890598

Replica Molding (REM)

- Uses a PDMS stamp as the master to duplicate molds. Polyurethane (PU) is then molded in the PDMS master.
- Sizes and shapes may be changed in a controlled way (mechanical compression, bending, or stretching).
- Ability to fabricate structures of ~30nm in organic polymers.

Replica Molding (REM)



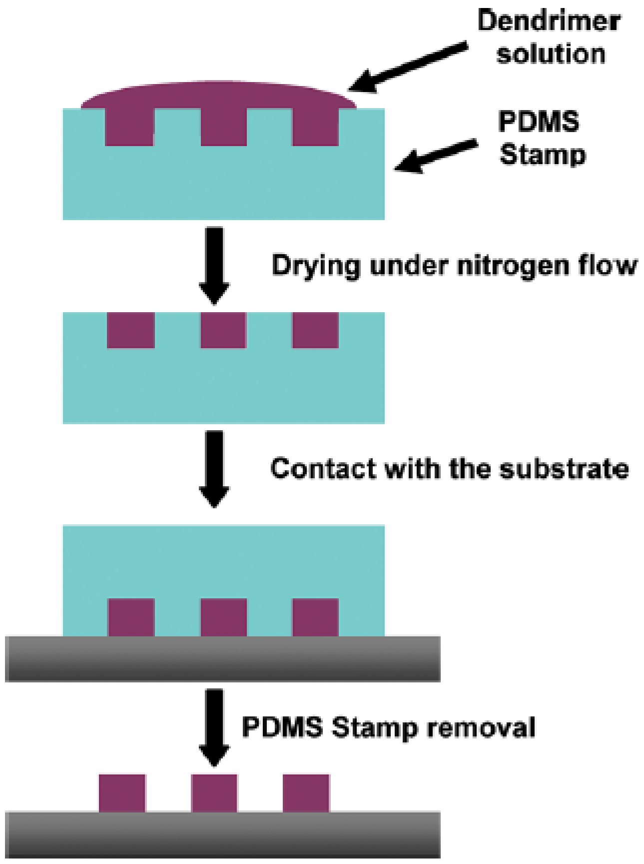
Edge lithography. (a) Schematic illustration of phase-shifting edge lithography using a PDMS stamp in contact with a photoresist. The schematic also illustrates the modulation of the light intensity at the interface between the PDMS stamp and the photoresist (i.e. the near-field region). This technique can pattern narrow linewidths as shown in the SEM image in (b) of 50 nm wide lines of positive-tone photoresist supported on Si. (Reproduced in part with permission from. © 2002 American Chemical Society.) (c) Schematic illustration of the fabrication of patterned arrays of conductive edges embedded in epoxy. The SEM image in (d) shows 50 nm wide Au edges exposed by sectioning the encapsulated structure with the glass knife of a microtome. (Reproduced in part with permission from. © 2004 American Chemical Society.)

Byron D. Gates
Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC V5A 1S6, Canada

Materials Today February 2005

Microtransfer Molding (μTM)

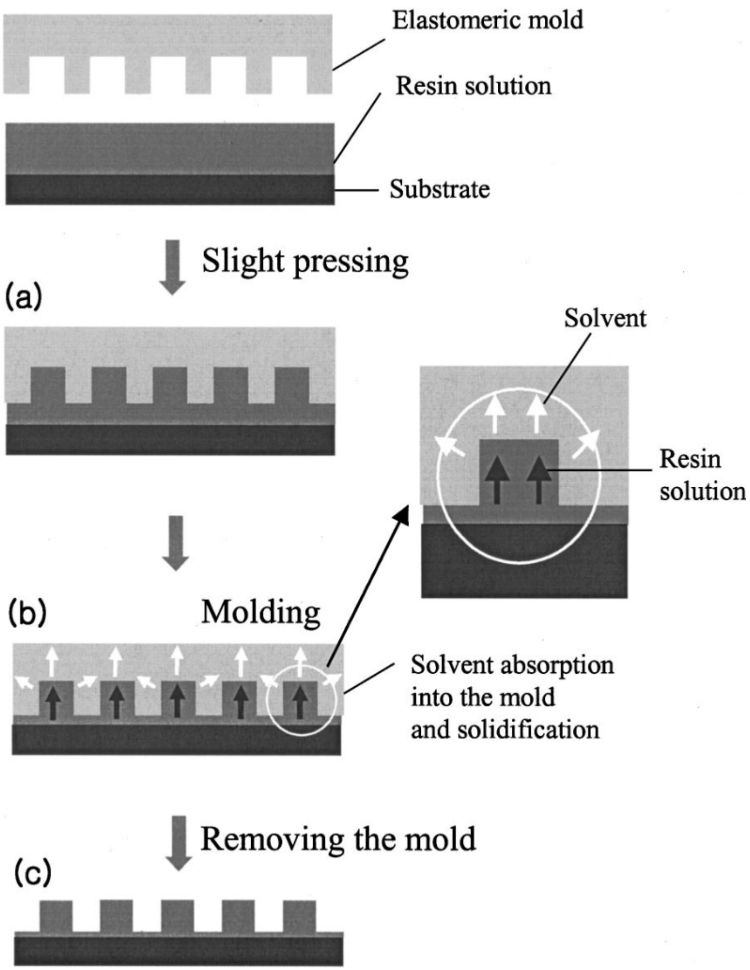
- A liquid prepolymer precursor is applied to the surface of a PDMS stamp. The excessive liquid is removed. The stamp is placed on the substrate and then, cured. The PDMS mold is then, peeled away.
- Structures as small as ~250nm.
- Between the raised structures a thin film is also formed from the precursor in the PDMS stamp.



Schematic procedure of microtransfer molding process.

C. Thibault et al. / Microelectronic Engineering 83 (2006) 1513–1516

Solvent-Assisted Micromolding (SAMIM)

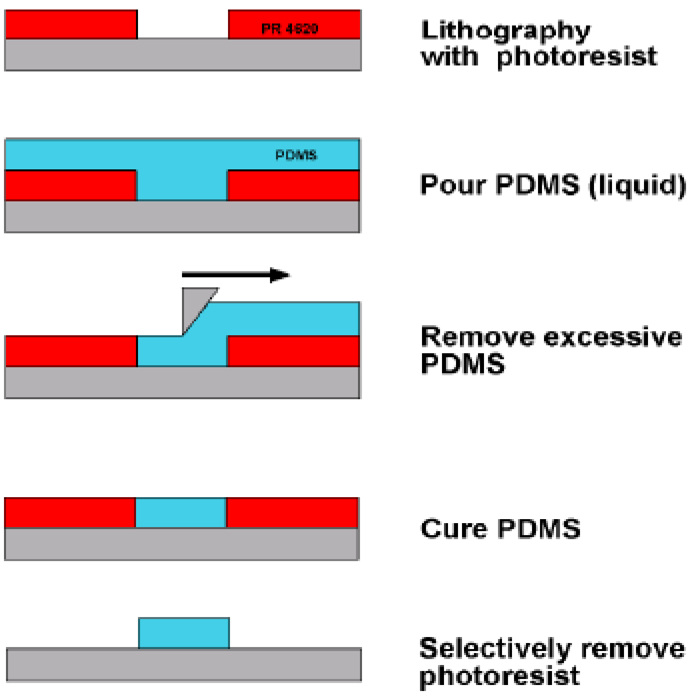


- Polymer solvent is spread on the PDMS stamp, which is brought into contact with a polymer film. The solvent dissolves or swells the polymer film.
- Small features of ~60nm (width) x ~50nm (height).
- The solvent should dissolve the polymer surface, but it should not dissolve, swell, or distort the PDMS stamp.

Appl. Phys. Lett., Vol. 79, No. 14, 1 October 2001

Fabricating PDMS Microfluidic Channels

- Lithography process - silicon substrate
- Apply SU-8, a negative photoresist (PR)
- Pour PDMS
- Remove excessive PDMS
- Thermal cure
- Selective removal of PR



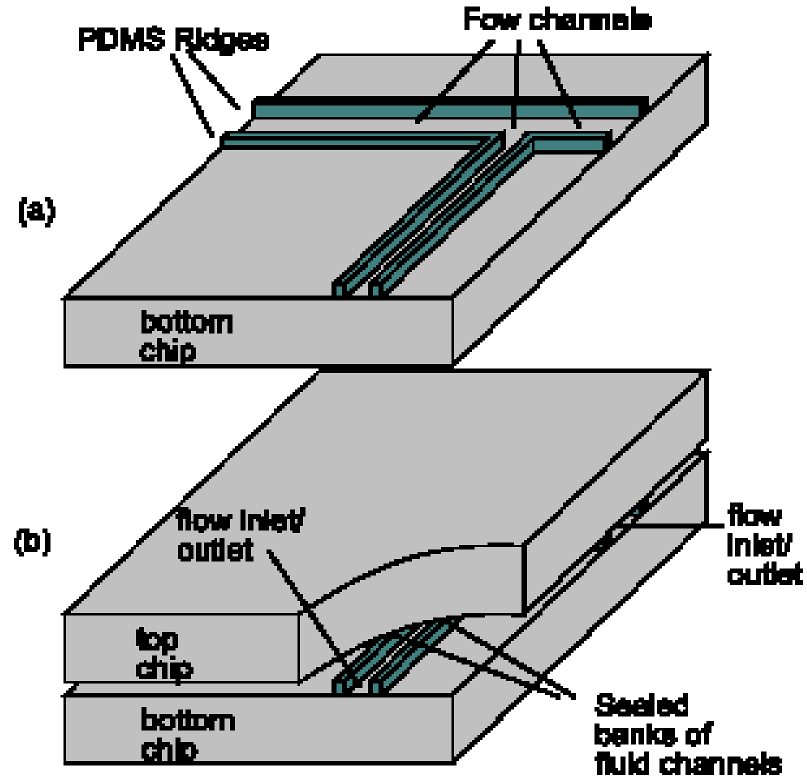
Schematic diagram illustrating the principle of forming/patterning PDMS thin film.

Ryu, K., Liu, Ch. "Precision Patterning of PDMS Thin Film: A New Fabrication Method and its applications"

Steps:

- The ridges of the patterned PDMS on the substrate forms the boundary of the fluidic channel

- The channels are formed by applying another substrate on top of the substrate containing the PDMS ridges.



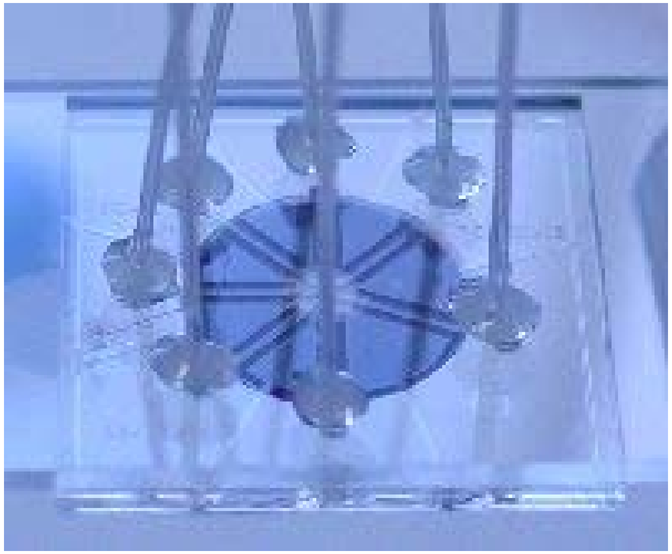
Schematic diagram illustrating the principle of forming microfluidic channel using PDMS micro patterning and soft bonding of two substrates. (a) PDMS patterns that define fluid channels are formed on the bottom substrate and then (b) sandwitched between two plates. The cutout in the top substrate to show the interior of the enclosed channels.

Ryu, K., Liu, Ch. “Precision Patterning of PDMS Thin Film: A New Fabrication Method and its applications”

PDMS Microfluidic Devices

Properties that make PDMS a well suited material for microfluidic devices:

- Biocompatibility
- High gas permeability
- Easy to fabricate complicated 3D microstructure



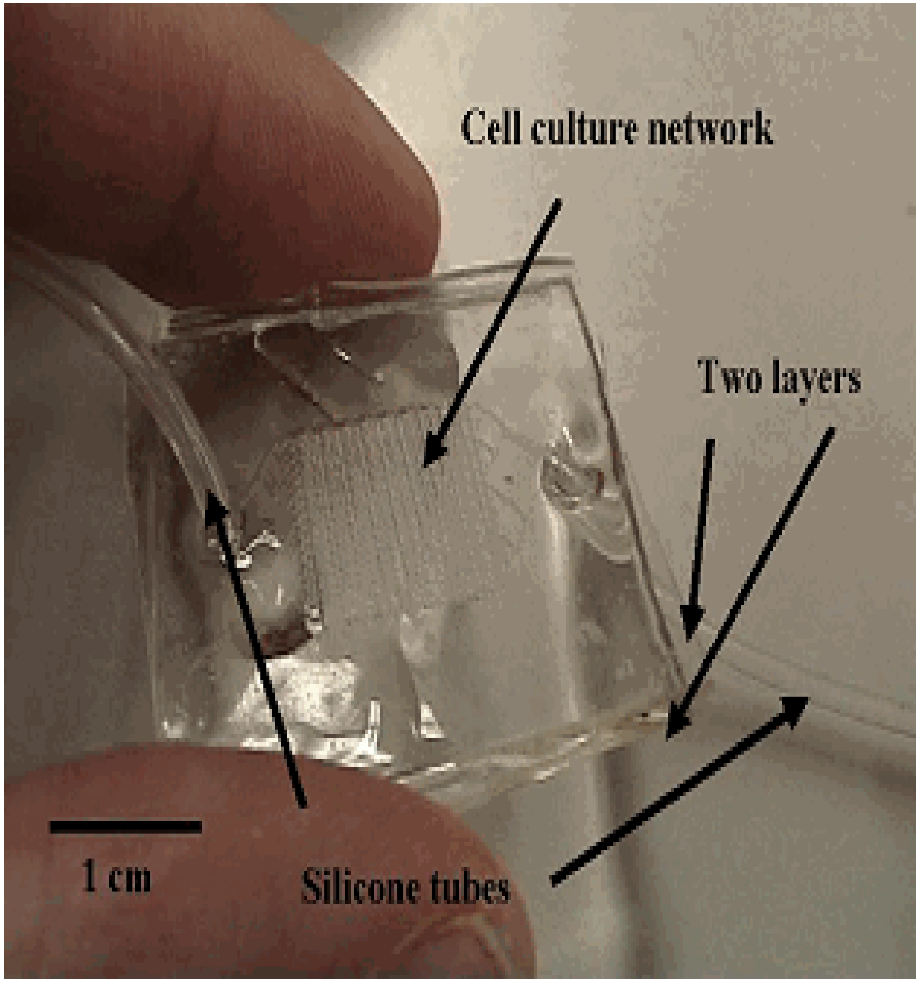
University of Hertfordshire. Microfluidics and Microengineering Group.

Application:

PDMS microfluidic devices with the embedded oxygen chamber provide a suitable environment for tissue cultures

PDMS Microfluidic Devices

1. Microfluidic structure
   (cell culture network)
   Composed of a channel network with two levels.
   -Inlet channels to distribute culture medium with uniform flow
   -channel for cell culture
2. Two layers of PDMS bond together to form the culture chamber (microchannel structure).



PDMS Microfluidic device

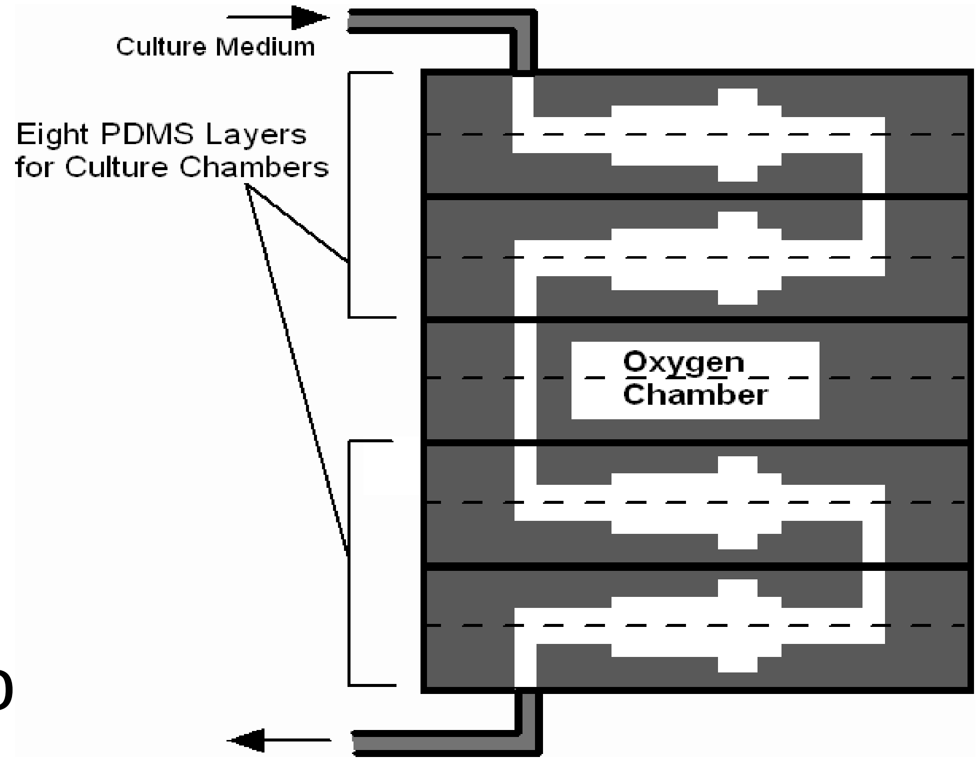
Cell Culture in 3-Dimensional Microfluidic Structure of PDMS polydimethylsil...
Eric Leclerc; Yasuyuki Sakai; Teruo Fujii *Biomedical Microdevices;* Jun 2003; 5, 2; Health Module pg. 109

Multilayer Microfluidic Device

- Stacking pairs of PDMS layers with oxygen chamber in between

-Oxygen chamber is opened to the atmosphere

-Oxygen is supplied into the culture chamber through PDMS layer

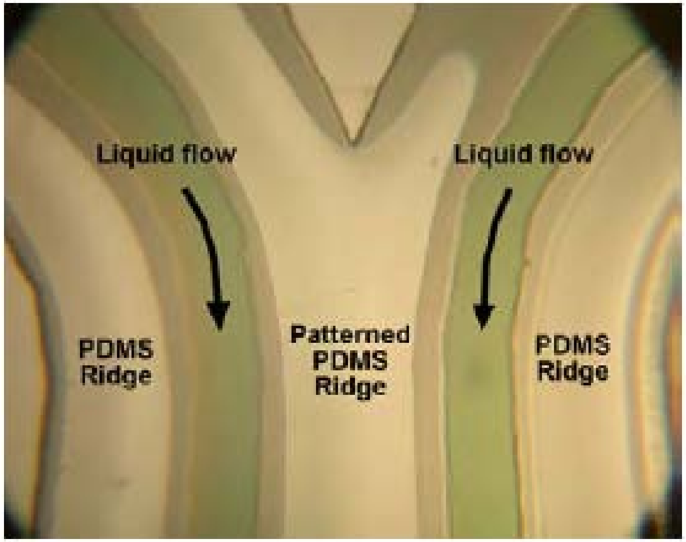


Structure of multilayer device

The Royal Society of Chemistry Lab Chip, 2006, 6, 1125–1139

Fabricating PDMS Microfluidic Channels

- An oxygen plasma treatment renders the channel hydrophilic allowing water based fluids to flow without the need for applying pressure.



Optical micrograph of two parallel fluid channels formed by the process shown in fig 2. Colored IPA solution runs in parallel fluid channels

Ryu, K., Liu, Ch. “Precision Patterning of PDMS Thin Film: A New Fabrication Method and its applications”

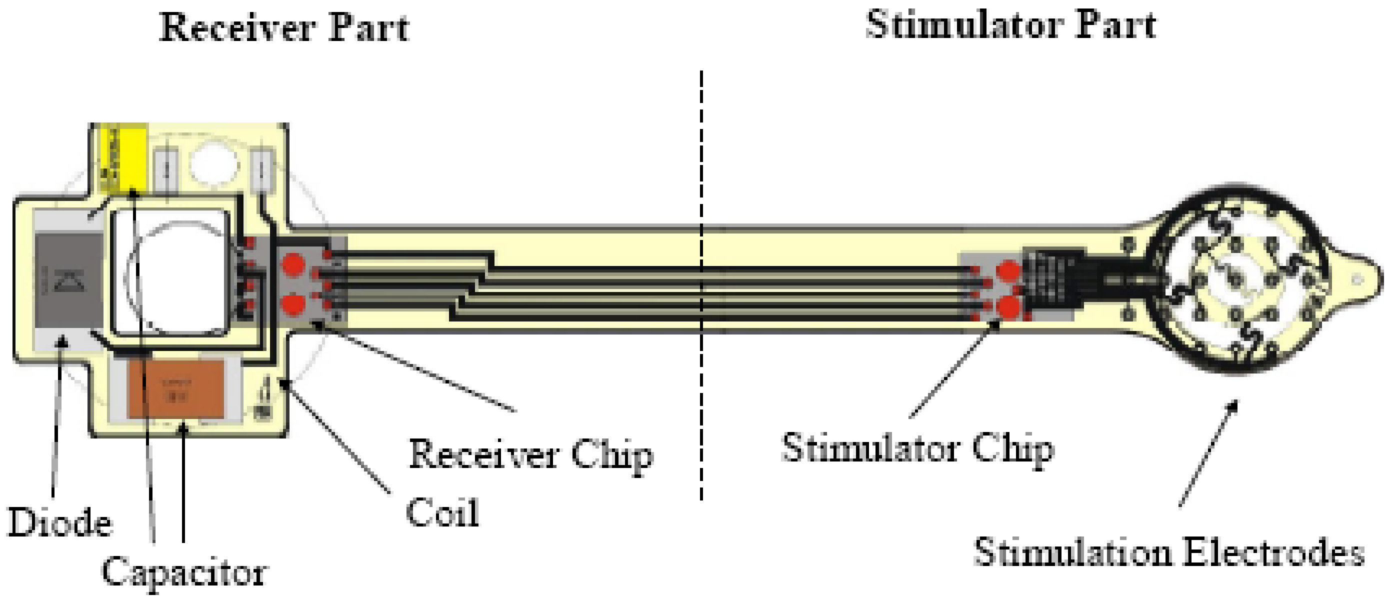
PDMS as Part of an Implanted Biomedical Microsystem

Retinal Prosthesis – Stimulating retinal neurons.

- A high dynamic range external CMOS camera sends images to an encoder in spatio-temporal stimulation patterns.
- These patterns match the input of the ganglion cell layer in an intact retina.
- A data decoding chip stimulates the proper retina cells electronically, which cause them to send action potentials to the brain via the optical nerve.

T. Stieglitz, W. Haberer, C. Lau, M. Goertz **Development of an Inductively Coupled Epiretinal Vision Prosthesis.** Proceedings of the 26th Annual International Conference of the IEEE EMBS San Francisco, CA, USA • September 1-5, 2004

PDMS as Part of an Implanted Biomedical Microsystem

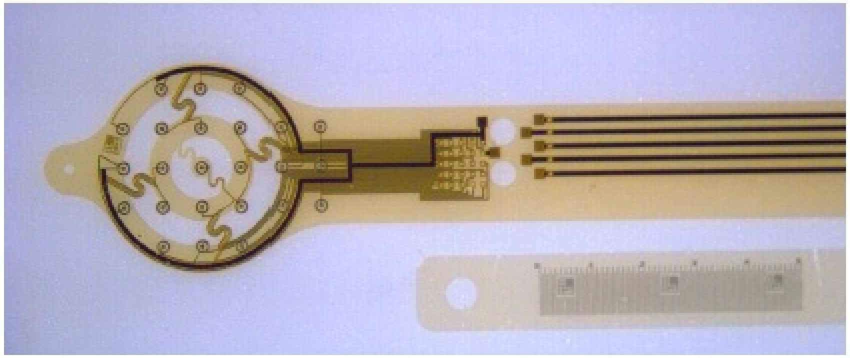


Design of an epiretinal vision prosthesis. Hybrid assembly of electronic components on a flexible substrate with monolithic integration of interconnects and stimulation electrodes.

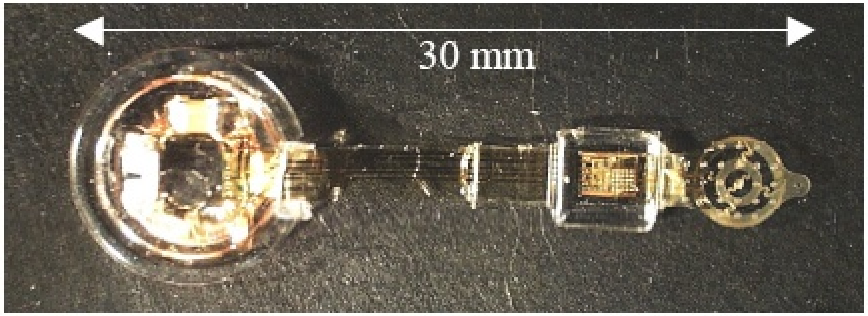
T. Stieglitz, W. Haberer, C. Lau, M. Goertz **Development of an Inductively Coupled Epiretinal Vision Prosthesis.** Proceedings of the 26th Annual International Conference of the IEEE EMBS San Francisco, CA, USA • September 1-5, 2004

PDMS as Part of an Implanted Biomedical Microsystem

- The retinal electrode array was synthesized on a flexible polyimide substrate with integrated platinum electrodes 15µm thick
- 50µm of PDMS encapsulated the entire device
- The device was implanted in a cat and resulted in a 2.5^{o} visual angel stimulation of the retina
- Only human patients will be able to determine if this technology will result in the blind being able to “see”



Electrode Array with integrated pad array for stimulation ASIC and interconnects; flexible polyimide substrate (Pyralin PI 2611, HD Microsystems) of 15 µm thickness with embedded platinum electrodes.



Epiretinal vision prosthesis with assembled electronic components after coating with parylene C and silicone encapsulation.

T. Stieglitz, W. Haberer, C. Lau, M. Goertz **Development of an Inductively Coupled Epiretinal Vision Prosthesis.** Proceedings of the 26th Annual International Conference of the IEEE EMBS San Francisco, CA, USA • September 1-5, 2004

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PDMS Modification

- Some PDMS applications require surface modification in order to improve the wettability and adhesion properties of PDMS surfaces.
  - Oxygen Plasma.
  - UV Light.
  - UV Light and Ozone (UVO).

Efimenko, K., Wallace, W. E., and Genzer, J. "Surface Modification of Sylgard-184 Poly(Dimethyl Diloxane) Networkds
by Ultraviolet and Ultraviolet/Ozone Treatment." *Journal of Colloid and Interface Science*. 2002, 254, 306-315.

Oxygen Plasma

- Reactive Ion Etch (RIE) oxygen plasma, has been the most widely used technique.
- Oxygen atoms substitute methyl groups on the PDMS surface leading to the formation of hydrophilic surfaces. Carbon pumped away as CO_2 and H_2O.
- Modified surfaces of PDMS can be used to bond glass, silicon substrates and other PDMS molds or structures

Efimenko, K., Wallace, W. E., and Genzer, J. "Surface Modification of Sylgard-184 Poly(Dimethyl Diloxane) Networkds by Ultraviolet and Ultraviolet/Ozone Treatment." *Journal of Colloid and Interface Science*. 2002, 254, 306-315.

UV Light and UV Light + Ozone (UVO)

- UV light increases Si-O concentration, forming a silica-like substrate.
- UVO is more effective than UV in creating hydrophilic groups because of the molecular oxygen and ozone present, which forms a larger number of hydrophilic species (OH).

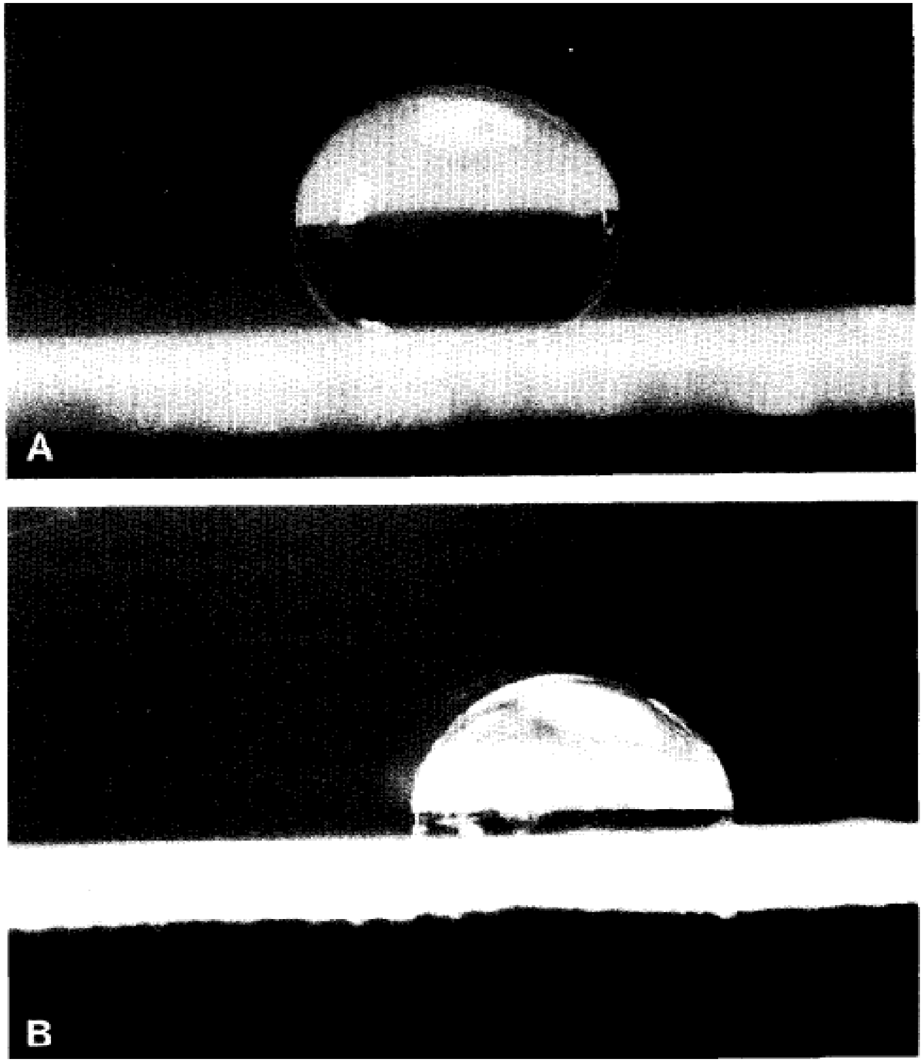
B. Schnyder et al. / Surface Science 532–535 (2003) 1067–1071

PDMS Treated with CO_2 Laser

Water drop on PDMS that was

A) treated with 3 pulses of the CO2 laser

B) untreated under a 50x objective [19].



Khorasani, Mirzadeh, and Sammes. Laser Induced Surface Modification of Polydimethylsiloxane as a Super-Hydrophobic Material. Radiat. Phys. Chem. Vol. 47, No. 6, pp. 881-888. Great Britain: Elsevier, 1996.

PDMS Bonding

Importance of PDMS bonding – Low temperature bonding

Bonding process : Standard lithography technique

- Spin deposition of PDMS
- Exposure with 420 nm Ultra Violet light
- Brief exposure to oxygen plasma cure (at 20 mTorr and 25W, for 20 seconds)
- Immediately join to glass, SiO2 or PDMS itself (with in 10 min)

Long exposure to plasma roughens the PDMS surface and interferes with bonding

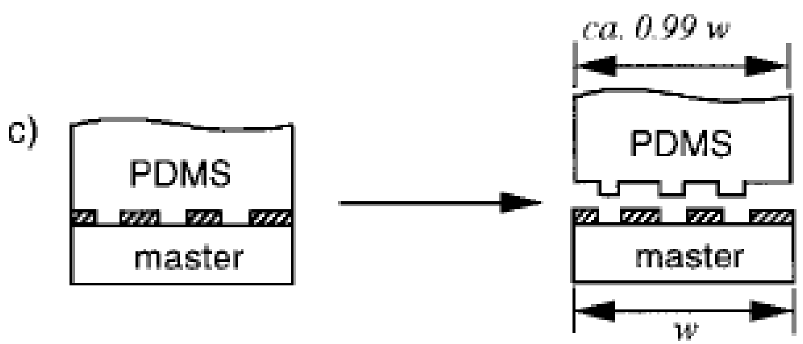
Advantages of PDMS

- Optical transparency (wavelength from 230 to 700nm makes it suitable for UV/ visible spectrophotometry).
- Permeable to variety of liquids and vapors (allows it to absorb a variety of compounds).
- Conforms to the surface of the substrate over a relatively large area
- Conformal contact achievable on nonplanar surfaces
- Can be released easily, even from complex and fragile structures
- Low cost.
- Simple fabrication process.

Disadvantages of PDMS

- Wide and shallow micro channels can easily collapse during the bonding process.
- Because PDMS is easily deformable, the technology is not well suited for devices that require precise pattern placement .
- PDMS stamps also tend to shrink to a factor of 1% upon curing.
- Some relief structures are not able to resist the compressive forces of printing and the adhesion between the stamp and the substrate, which leads to sagging.

Disadvantages of PDMS



a. Collapsing / Paring

b. Sagging

c. Shrinking

J. Am. Chem. Soc. **1996,** *118,* 5722-5731

Summary of PDMS

- 70 year technology with present and future applications in micro and nanofabrication such as microfluidics and biomedical applications
- Spun, wiped or pour deposited
- Heat decreased curing time
- Soft, pliable, clear, safe, easy to use and inexpensive
- 24 month shelf life from date of manufacture