Microcontact Printing (μCP)

Maddison Coca and Prof. Steven Baldelli

Department of Chemistry, University of Houston, Houston, Texas

Introduction

Microcontact printing (μCP) is a technique rooted in soft lithography (the process of creating a relief pattern on a substrate using an elastomeric stamp) and has a multitude of applications. Soft lithography is widely used in microfluidics, microelectronics, and biotechnology for creating microarray technology. The patterned elastomeric stamp used in the process of microcontact printing (μCP) transfers ink such as proteins, polymers, or nanoparticles to the surface of a substrate allowing for the examination of how molecules react on a specific surface. A few different processes of microcontact printing (μCP) are decomposition of metals by chemical vapor deposition, electroplating, electroless plating, protein microarrays, and substrates that are capable of analyzing antigen antibody interactions (antigen antibody interactions are interactions between protective proteins replicated by the immune system (antibodies) and their attachment to bacteria, fungi, & viruses (antigens)). Some of the fields microcontact printing (μCP) is used for:

Increasing crop yield
- fertilizers
- plant growth stimulators
- soil improvers

Nanobiotechnology
- target genetic engeneering
- biomolecule delivery
- monitoring physiological processes

Nanoencapsulation
- slow-release fertilizers pesticides, herbicides
- triggered-release capsules

Sorbents
- pollutant removal
- soil remediation
- water purification

Plant protection
active constituents for:
- pesticides
- herbicides
- insecticides

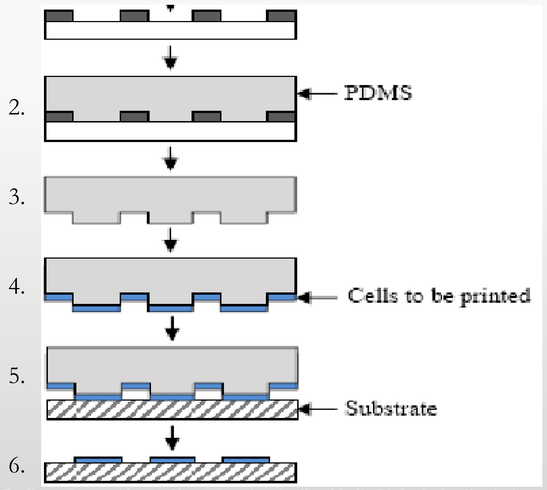
Environmental sensing
- soil conditions
- contamonant concentration
- crop diagnostics

Antimicrobal agents
- water desinfection
- antimicrobal surface coating

Renewable energy
- solar energy collection
- wind harvesting devices
- energy storage

Sajid, Muhammad, and Justyna Płotka-Wasylka. "Nanoparticles: Synthesis, Characteristics, and Applications in Analytical and Other Sciences." Microchemical Journal, vol. 154, May 2020, p. 104623. https://doi.org/10.1016/j.microc.2020.104623.

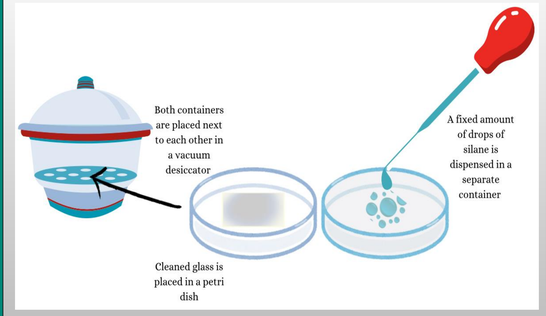
Experiment



Faulkner-Jones, Alan & Shu, Wenmiao (Will). (2012). Biological cell printing technologies. Nanotechnology Perceptions. 8. 35-57. 10.4024/N02FA12A.ntp.08.01.

- Trichloroperfluorooctyl silane is applied to the surface of a substrate through the use of a vacuum desiccator
- A polydimethylsiloxane (PDMS) stamp is made and poured over substrate
- Cured stamp is peeled away from substrate, forming a relief pattern from the patterned silane hydrophobic film
- Octadecanethiol (ODT) is doused onto stamp, known as "inking", and dried with a stream of nitrogen gas
- The octadecanethiol (ODT) cells are pressed onto gold for a fixed amount of time
- When the stamp is removed from the gold, self-assembled monolayers (SAMs) are left behind
- Bare gold from the area where the stamp did not make contact with the gold is etched away in a solution of KOH and KCN

Applying Silane to Glass Surface

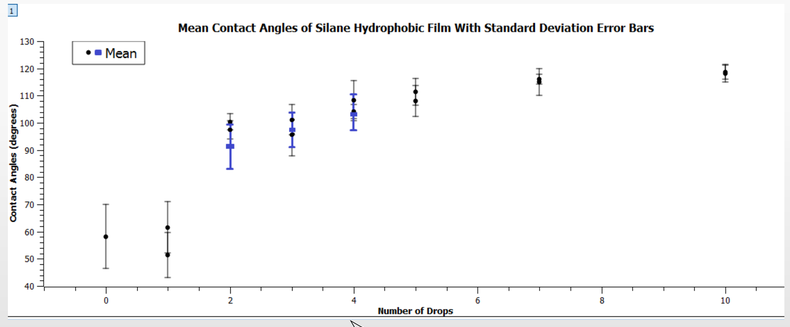


What does a vacuum desiccator do?
Vaporizes the silane and forms a monolayer on the surface of a substrate. This monolayer prevents the PDMS stamp from adhering to the substrate and controls surface energy that influences wetting properties (hydrophobicity/hydrophilicity) and interactions.

What is the goal of the silane film?
Achieve average contact angles of 110-115 degrees, with the potential to have higher angles, that provide the best protective barrier while maintaining a transparent film on the substrate surface.

Method
- Experimented with the number of drops (results below).
- Time samples were left in the vacuum desiccator were kept constant at 30 minutes.
- Took samples out carefully and measured contact angles of the glass.

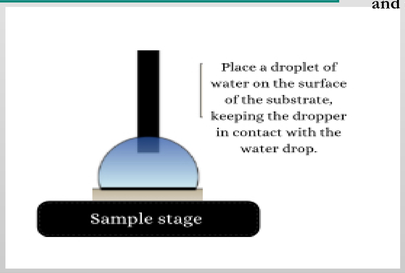
Measuring & Computing Contact Angles of Silane Film

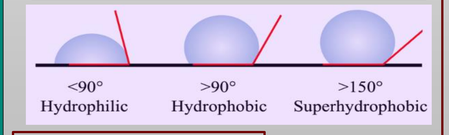


What this graph means
- Graphical representation of the variability of experiments performed.
- Contact angles steadily increase as the number of drops of silane increases, but eventually level out after seven drops.

➢ Error bars that are in blue represent oven cleaned glass
➢ Graph was fabricated in SciDAVis and is based on the contact angles of both the left and right side found in ImageJ

Method of Checking Wettability

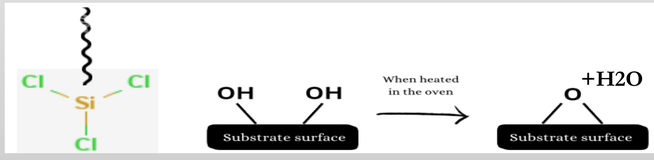




The silane film applied to the glass surface through vaporization makes the surface hydrophobic.

Entomological Society of America. (2024, February 22). *Contact angles*. Entomology Today.

Why Oven Cleaned Glass Produced Lower Contact Angles



SiCl3 hydrolyzes in the presence of moisture to form silanol groups (Si-OH). The chlorine atoms are replaced by a hydroxyl group (OH), resulting in Si-OH and hydrochloric acid (HCl).

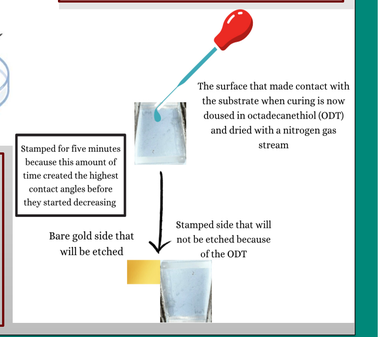
The silanol groups can condense and form strong bonds with the hydroxyl groups already on the glass surface. This is how the hydrophobic film is created.

However, when heating occurs, the OH groups on the glass' surface breaks down a nd forms oxygen plus water, which decreases the intensity of hydrophobicity applied to the surface.

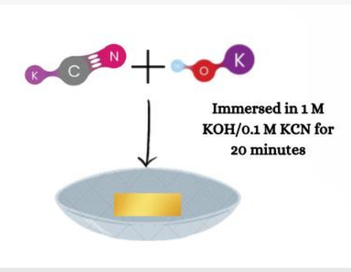
PDMS Stamp

What does the ODT do?
Octadecanethiol is often used to create self-assembled monolayers (SAMs) on a substrate surface. The SAMs that form with octadecanethiol alters the chemical and physical behaviors, like hydrophobicity, as well as resistance to corrosion (etching).

Curing the PDMS stamp
Put petri dish with glass substrate and PDMS solution in a vacuum oven for two hours with only heat (60 degrees Celsius).

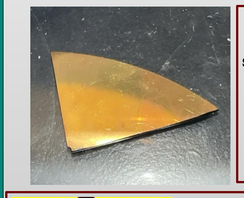


Etching

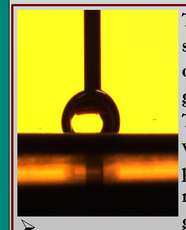


What is the role of KOH and KCN?
- KOH etches at different rates (anisotropic) allowing for controllable etch rates.
- KCN etches material in all directions uniformly (isotropic) and is specifically used in gold etching because it forms soluble gold cyanide complexes, enabling the gold to dissolve.

Results

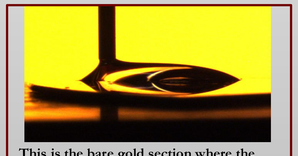


On the left side is where the PDMS stamp made contact with the gold and on the right side is where the PDMS stamp did not make contact with the gold, allowing KOH/KCN to etch away the bare gold.



➢ Left: 100.1 degrees & Right: 97.0 degrees

This is the stamped part of the gold. The ODT acted as a wet-etch protection making the gold in this area stay hydrophobic.



This is the bare gold section where the stamp made no contact after being doused in ODT. Since there was no protection barrier being provided by the ODT, the gold was essentially corroded away from the etchants, making it hydrophilic.

➢ Left: 41.6 degrees & Right: 48.1 degrees

Conclusion

Special thanks to Elora Zucha and Professor Steven Baldelli

- ✓ Seven and ten drops of silane produced similar contact angles on the surface of glass, meaning both surface compositions are suitable for providing adhering protection and affecting wettability in the form of hydrophobicity.
- ✓ The relationship between number of drops of silane and contact angles is proportional as seen in the graph's gradual increase and leveling out of contact angles.
- ✓ Oven cleaned glass produced lower contact angles than other samples that were not put in the oven because of the decomposition of OH on the surface of glass when heating, making the film less applicable.
- ✓ Making a PDMS stamp worthy of stamping the gold with octadecanethiol without any impurities meant heating the stamp in a vacuum oven at 60 degrees Celsius for two hours.
- ✓ Immersing gold in higher concentrations of KOH/KCN etched away the gold better, achieving a hydrophobic side from the protective layer of octadecanethiol and a hydrophilic side from the corrosion of bare gold without octadecanethiol.