EWOD: Theory and fabrication

Gaurav J. Shah
Sofie Biosciences
Visiting Scientist, Mike van Dam Lab
4/24/13

Outline

- Recap: background
- Electrowetting-on-dielectric theory
  - Thermodynamic: historic view, convenient ‘shorthand’
  - Electromechanical : more recent, rigorous and accurate
- Device fabrication
  - Process flow and steps
  - Some key considerations
- Cleanroom tour

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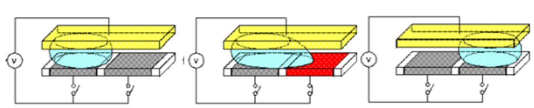
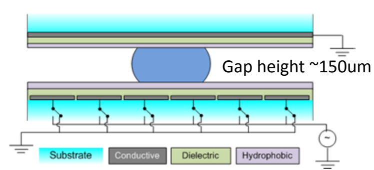
Parallel plate configuration for EWOD “digital microfluidics”

“Digital” : discrete packets or droplets of liquid (as opposed to channel flow)





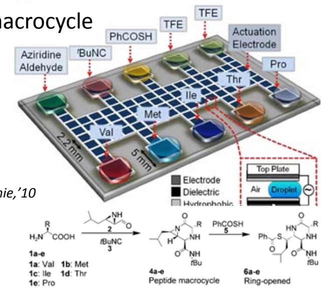
Typical parallel-plate EWOD device

- Electrode array buried under dielectric layer and hydrophobic coating
  - Ground wire replaced by cover plate with ground plane
- Droplet operations controlled by voltage sequence applied to electrodes
  - creation (from larger reservoir)
  - transport
  - merging
  - mixing
  - splitting

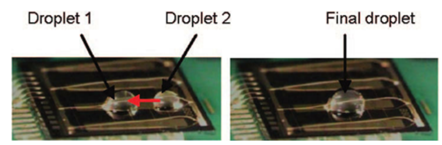
Moon, UTA

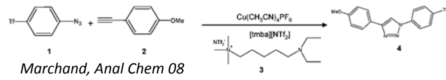
(Bio)chemistry on digital microfluidics

Peptide macrocycle synthesis



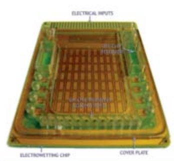
Jebrail, AWchemie,'10

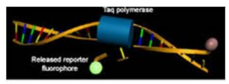




Marchand, Anal Chem 08

Click chemistry in ionic liquids



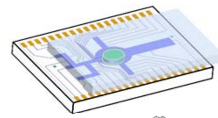


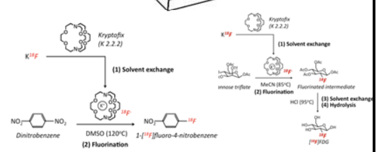
Sista LoC '08

Real-time Polymerase chain reaction

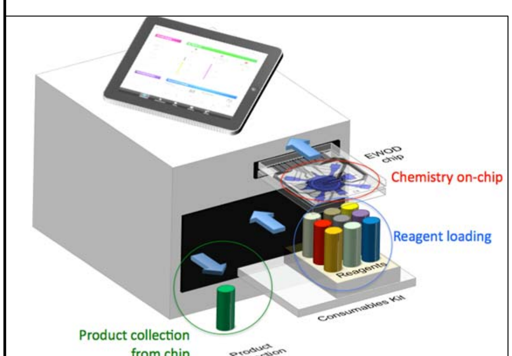
Radiochemical synthesis

Chen, Hilton Head 2010, Keng, PNAS 2012





Motivation: Radiochemistry on EWOD



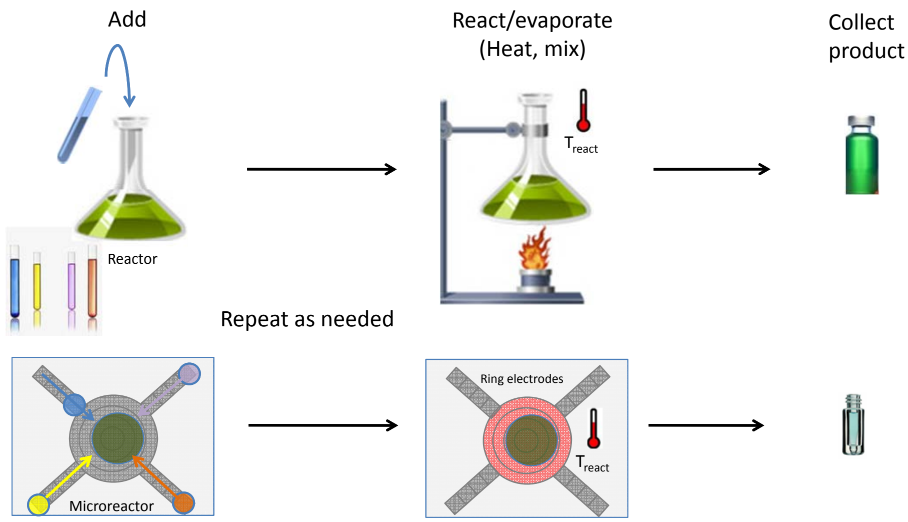
Key advantages:
Compact: towards automated benchtop radiosynthesizer

Open structure allows faster evaporation

Material compatibility (vs. PDMS devices)

Chemistry using digital microfluidics

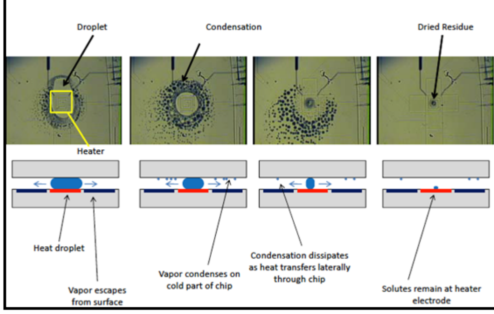
Mimicking macroscale chemical reactions



Objective: Digital microfluidics based automated platform to perform these operations

Radiochemistry on EWOD platform

16x speed



- Each step consists of reagent loading, transport and heating
- Electrically controlled resistive heating can be incorporataed on chip
- Open configuration allows faster evaporation for azeotropic drying

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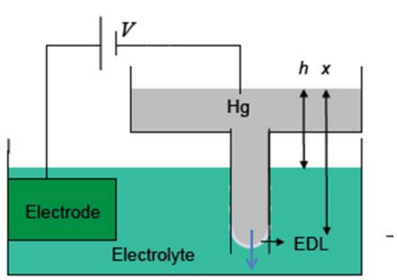
Electrowetting: a brief history

- Lippman’s experiment on “Electrocapillarity” (1875)
  - Experimentally observed a “decrease in surface tension with applied potential” to mercury column
  - Related it to the charge accumulated at the interface (Electric double layer or EDL)



Force balance of the system:

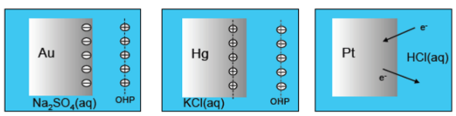
$$\rho_m g x A = \rho_e g (x-h) A + \gamma P$$

$$\rightarrow \Delta\gamma = \frac{(\rho_m - \rho_e) g A}{P} \Delta x$$

Recap: Electric double layer

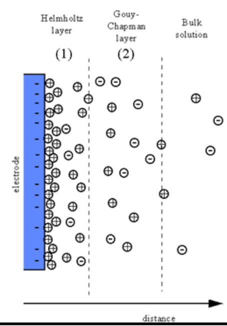
- A polarizable surface in contact with an electrolyte becomes charged
  - Charge could be positive or negative (or surface could be non-polarizable)
- A charged surface in contact with an electrolyte leads to charge redistribution near the interface: Electric Double Layer (EDL)
- Typical thickness ~ 1-10nm
- EDL can sustain a small electrical potential across it

➔ Acts like a small capacitor



Example of the polarizable and non-polarizable interfaces

PZC: potential of zero charge $\Phi = V - V_{PZC}$



Lippmann Equation

- Above PZC, (effective) change in surface tension, Δγ, is proportional to V^2

$$\frac{d\gamma}{d\Phi} = -\frac{Q}{A} = -q = -c\Phi$$

c: capacitance per unit area of EDL

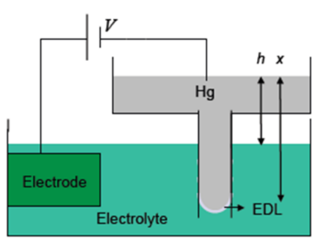
$$\gamma = \gamma_0 - \frac{1}{2}c\Phi^2$$

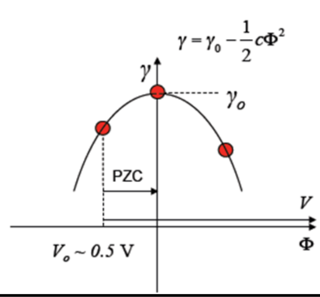
Lippmann Equation

PZC: potential of zero charge

$$\Phi = V - V_{PZC}$$

$$\gamma = \gamma_0 - \frac{1}{2}c(V - V_{PZC})^2$$





Electrocapillarity → Electrowetting

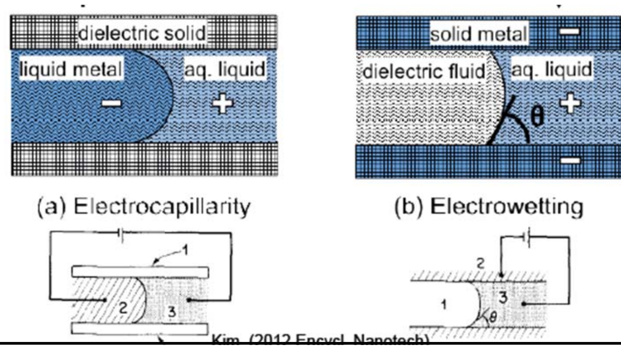
- Electrocapillarity: potential across a liquid-liquid interface

➔ **$\gamma_{ll'}$ changes**

- Electrowetting (EW): potential across solid-liquid interface

→ **γ_{sl} changes**

  - First shown in 1981 by Beni et al.
  - Leads to decrease in contact angle (wetting) of liquid on solid



Kim (2012 Encycl. Nanotech)

EW induced contact angle change

- Relates contact angle change to interface potential
  - Young's Equation is force balance of surface tensions in the x-direction

Young's Equation:

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv}\cos\theta$$

Lippmann Equation:

$$\gamma_{sl}(\Phi) = \gamma_{sl}(0) - \frac{1}{2}c\Phi^2$$

Lippmann-Young equation:

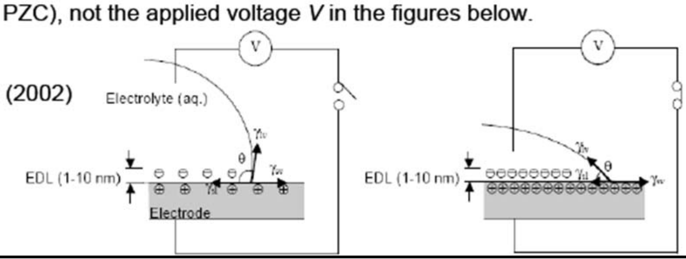
$$\cos(\theta(\Phi)) = \cos\theta_0 + \frac{1}{2\gamma_{lv}}c\Phi^2$$

Note: the voltage Φ in the equations is the potential at the interface (i.e., potential difference from PZC), not the applied voltage V in the figures below.

Moon and Kim (2002)

PZC: potential of zero charge

$\Phi = V - V_{PZC}$



EW→Electrowetting-on-dielectric (EWOD): Why on-dielectric?

- EW only across EDL has limited force (effectiveness)
  - Only small potential (Φ) is applicable before EDL breakdown and current leakage
    → Only small contact angle change can be achieved
  - Contact angle change tends to be irreversible

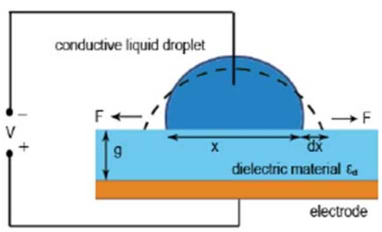
Lippmann-Young equation:

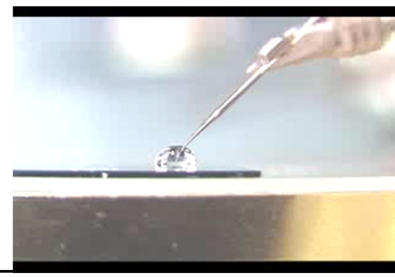
$$\cos(\theta(\Phi)) = \cos\theta_0 + \frac{1}{2\gamma_{lv}} c\Phi^2$$

- Dielectric layer is employed to improve reversibility of electrowetting:
  - Higher voltage can be sustained: large force
  - Reversible process

PZC: potential of zero charge

$$\Phi = V - V_{PZC}$$





Lippmann-Young Equation for EWOD

$$\cos(\theta(\Phi)) = \cos\theta_0 + \frac{1}{2\gamma_{lv}} c\Phi^2$$

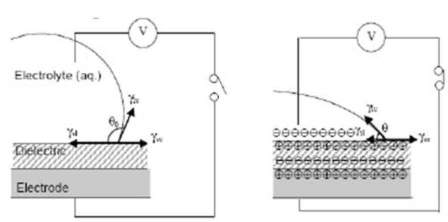
Since PZC ~ 0, the Φ in the equation equals the applied voltage V in the figures

$$\cos(\theta(V)) = \cos\theta_0 + \frac{1}{2\gamma_{lv}} cV^2 = \cos\theta_0 + \frac{1}{2\gamma_{lv}} \frac{\varepsilon_d \varepsilon_0}{d} V^2$$

Specific capacitance, *c* (per unit area)

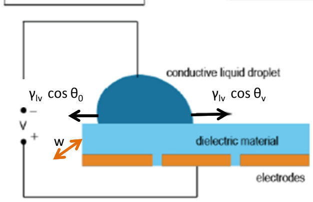
PZC: potential of zero charge

$$\Phi = V - V_{PZC}$$



EWOD Force:

$$F = \gamma_{lv} w \cdot (\cos\theta(V) - \cos\theta_0) = \tfrac{w}{2}\left(\tfrac{\varepsilon_d \varepsilon_0}{d} V^2\right)$$

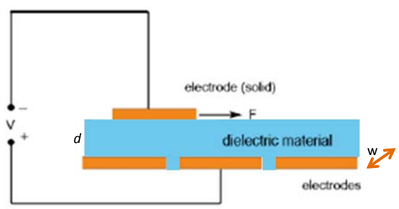


Note:

1. Droplet is assumed to be conductive→ no voltage drop across it
2. Usually there is also a thin hydrophobic layer between dielectric and droplet
   - Much thinner than dielectric→ contributes little to capacitance
3. The more common EWOD configuration used in EWOD microfluidics replaces the ground wire with a ground plane (reference electrode)

Electromechanical interpretation of EWOD

- Consider a electrode plate that can move in parallel

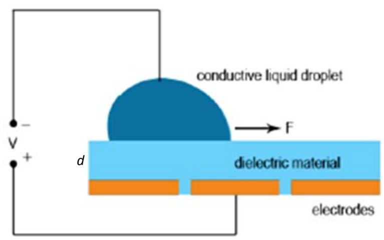


Electrostatic force:

$$F = -\frac{\partial U}{dx} = -\frac{\partial}{\partial x}\left(-\frac{A}{2}\left(\frac{\varepsilon_d \varepsilon_0}{d}V^2\right)\right) = -\frac{\partial}{\partial x}\left(-\frac{wx}{2}\left(\frac{\varepsilon_d \varepsilon_0}{d}V^2\right)\right)$$

$$F = \frac{w}{2}\left(\frac{\varepsilon_d \varepsilon_0}{d}V^2\right) = \frac{w}{2}(cV^2)$$

- Consider a conductive liquid droplet that can slide on dielectric surface



EWOD force (as found by Lipmmann Young Eq.) :

$$F = \gamma_{lv} w \cdot (\cos\theta(V) - \cos\theta_0)$$

$$F = \frac{w}{2}\left(\frac{\varepsilon_d \varepsilon_0}{d}V^2\right) = \frac{w}{2}(cV^2)$$

Lippmann equation leads to the same exact expression as the electrostatic force!

Thermodynamic vs electromechanical

Q. Which is more accurate depiction of physics?

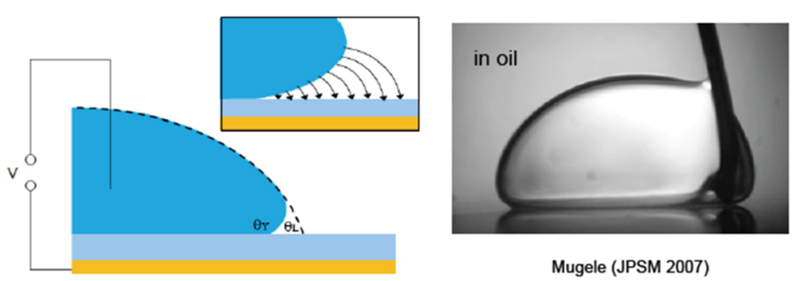
- If Thermodynamic theory:
  - Electrowetting is described as electrical control of surface tension
  - Contact angle reduction is understood as the **cause** of interface moving
  - Surface tension is the driving force
- If Electromechanical theory:
  - Electrowetting force originates from electromechanical force
  - Contact angle reduction is understood as the **result** of electromechanical force
  - Electrostatic force is the driving force

Why is this question significant?

- Esp. in radiochemistry, several non-aqueous liquids used
  - Contact angle change is much smaller than water, if any!
  - MeCN, MeOH, DMSO, etc.
- Will EWOD work for these non-aqueous liquids?
  - Based on thermodynamic view : no
  - Based on electromechanical view: maybe!

Electromechanical view "wins"!

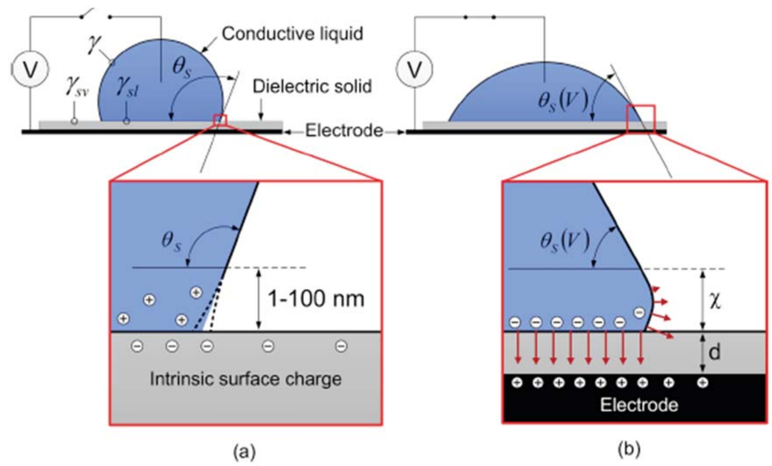
- Recent theoretical studies and experimental observations show electromechanical interpretation is more accurate
- Electrical field is concentrated near the meniscus, causing the deformation of droplet ➔ Macroscopic contact angle changes as a consequence
- The **microscopic** contact angle right on the contact line remains Young's contact angle (independent of the applied voltage)



Mugele (JPSM 2007)

Contact angle change is only apparent!

At scales on the order of dielectric thickness, contact angle is unchanged!
➔ Not really **"electrowetting"!** But a convenient shorthand; name stays



The static contact angle of a conductive liquid on an EWOD surface surrounded by a dielectric fluid (a) under no voltage and (b) under voltage. For the boxed drawings enlarged for the contact line region, (a) is more magnified than (b). In (b), χ is on the order of d, which is on the order of 1 μm in many EWOD devices.

Nelson, Kim (JAST 2012)

Revised thermodynamic view of EWOD:
Effective or equivalent surface tension change

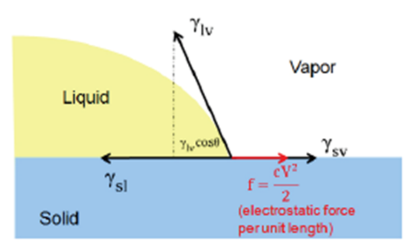
Electromechanical force balance at the three phase contact line:

$$\gamma_{sl} + \gamma_{lv}\cos(\theta(V)) = \gamma_{sv} + f$$

$$f = \frac{1}{2}cV^2$$

$$\gamma_{sl} + \gamma_{lv}\cos\theta_o = \gamma_{sv}$$

$$\rightarrow \cos(\theta(V)) = \cos\theta_o + \frac{1}{2\gamma_{lv}}cV^2$$



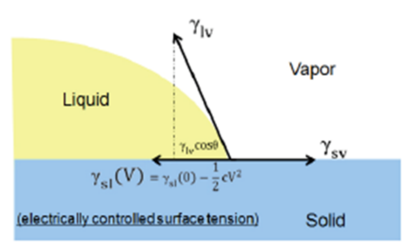
Thermodynamic force balance at the three phase contact line:

$$\gamma_{sl}(V) + \gamma_{lv}\cos(\theta(V)) = \gamma_{sv}$$

$$\gamma_{sl}(V) = \gamma_{sl} - \frac{1}{2}cV^2$$

$$\gamma_{sl} + \gamma_{lv}\cos\theta_0 = \gamma_{sv}$$

$$\rightarrow \cos(\theta(V)) = \cos\theta_0 + \frac{1}{2\gamma_{lv}}cV^2$$



Equivalent surface tension

Non-aqueous liquids can indeed be moved

Note 1: Even with contact angle change much smaller than water, liquids moved!

Table 1 Organic solvent and solution droplet movement feasibility

Liquid	μ/D[a]	k_d[a]	σ/S m^{-1}[a]	γ/dynes cm^{-1}[a]	$\Delta\theta/°$[a]	Movable[b]
Formamide	3.7	111	3.5×10^{-3} [52]	57	16.1 ± 0.4*	Y
Water	1.9	80.1	8.7×10^{-4}*	72	30.0 ± 0*	Y
Formic acid	1.4	51.1	7×10^{-3} [53]	37	26.3 ± 2*	Y
DMSO	4	47.2	3×10^{-5} [52]	43	15.3 ± 0.3*	Y
DMF	3.8	38.3	3.2×10^{-5} [52]	37	6.9 ± 2*	Y
Acetonitrile	3.9	36.6	1.9×10^{-5} [52]	29	9.8 ± 0.6*	Y
Methanol	1.7	33	1.7×10^{-4}*	22	9.8 ± 1*	Y
Ethanol	1.7	25.3	7.4×10^{-5}*	22	10.5 ± 0.7*	Y
Acetone	2.9	21	5×10^{-7} [54]	23	6.4 ± 0.2*	Y
Piperidine	1.2	4.3	1×10^{-5} [55]	29	8.9 ± 0.6*	Y
1-Pentanol	1.7	15.1	8×10^{-7} [56]	25	12.8 ± 0.8*	Y◇
1-Hexanol	1.8	13	1.6×10^{5}*	26	14.6 ± 0.7*	Y◇
Dichloromethane	1.6	8.9	1×10^{-7} [57]	27	3.7 ± 0.6*	Y◇
Dibromomethane	1.4	7.8	2.6×10^{-6}*	39	7.3 ± 1*	Y◇
THF	1.6	7.5	5×10^{-8}*	26[58]	4.9 ± 0.9*	Y◇
m-Dichlorobenzene	1.7	5		35	0.1 ± 0.1*	Y◇
Chloroform	1	4.8	7×10^{-8} [57]	27	0.5 ± 0.4*	Y◇
65% Toluene, 35% 1-hexanol	1.1§	3.7*	3×10^{-8}*	28*	6.1 ± 3*	Y◇
70% Toluene, 30% 1-hexanol	1§	3.4*		28*	0.3 ± 0.3*	Y◇
4-Methyl-3-heptanol	1.23	3.3		25[59]	0.1 ± 0.3*	Y◇
75% Toluene, 25% 1-hexanol	0.9§	3.1*		28*	0.0 ± 0.2*	Y◇
4.7 mM TBATFB in toluene		2.3*	1.8×10^{-7}*	28*	5.6 ± 0.6*	Y◇
80% Toluene, 20% 1-hexanol	0.8§	2.9*		28*	0.1 ± 0.3*	N
4-Methyl-4-heptanol		2.9		25[60]	0.2 ± 0.2*	N
Toluene	0.4	2.4*	8×10^{-14} [58]	28	0.2 ± 0.4*	N
Carbon tetrachloride	0	2.2	4×10^{-16} [58]	26	1.0 ± 0.0*	N
Cyclohexane	0	2	7×10^{-16} [58]	25	0.2 ± 0.5*	N
Decane	0	1.8*		23	0.5 ± 0.6*	N
p-Dichlorobenzene dissolved in toluene		1.5*				N

Always move

Move only at lower freq. or smaller gap

Do not move

Chatterjee, 2006 LabChip

Tested with 90Vrms, 10-8000Hz, 50-300um gap

Note 2: Some liquids move only at higher frequencies->Dielectrophoresis (DEP) force too (next)

Note 3: Some liquids never moved→ non-polar liquids; but MAY move at higher voltages!

EWOD using AC potential: EWOD and DEP

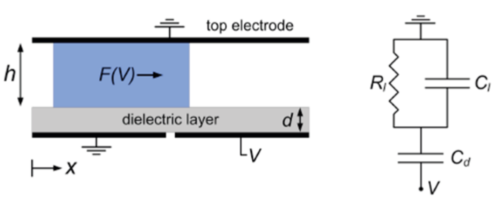
- **With DC** (f=0 Hz): liquid is a resistor in series with dielectric (capacitor) → No current at steady state

  → **No V in liquid**; all V is across the dielectric capacitance→ Only EWOD
- **For AC** (f>0Hz): voltage is more complex due to finite conductivity and dielectric constant.

  → **Voltage distributed** between liquid and dielectric→ Both EWOD and DEP

  Ratio of voltage across each depends on frequency of ac

Liquid impedance Z_l = R//C



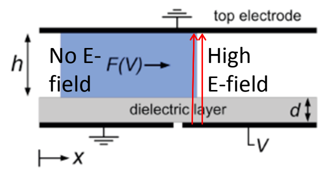
$$Z \equiv \frac{d}{A}\left(\frac{\rho}{1+\rho^2\varepsilon_0^2\varepsilon_r^2\omega^2} - j\frac{\rho^2\varepsilon_0\varepsilon_r\omega}{1+\rho^2\varepsilon_0^2\varepsilon_r^2\omega^2}\right)$$

→ Liquid impedance Z_l and dielectric impedance Z_d are both frequency-dependent

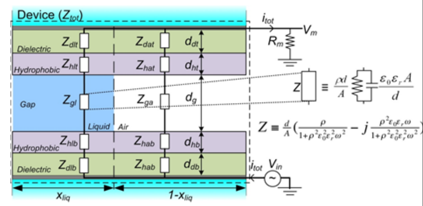
Simplified lumped RC circuit model

Voltage across the liquid produced Dielectrophoresis (DEP) force

- DEP: force exerted on dielectric particles in a non-uniform electric field
  - Droplet experiences positive DEP→ moves towards higher E-field



- In AC electrowetting, both EWOD and DEP contribute to actuation
- Contributions depend on:
  - the electrical properties and geometry of each layer
  - Actuation frequency



Lumped RC circuit model for 2-plate configuration

Summary: Theory

- EWOD is essentially electrostatic fluidic actuation
  - Only apparently wetting, but electrowetting name has stuck!
  - Enables "digital microfluidics"
    - discrete droplets with individually controllable paths
- Depending on actuation frequency, a combination of EWOD and DEP forces drive droplets
  - Aqueous and organic reagents can be actuated as required in radiochemistry

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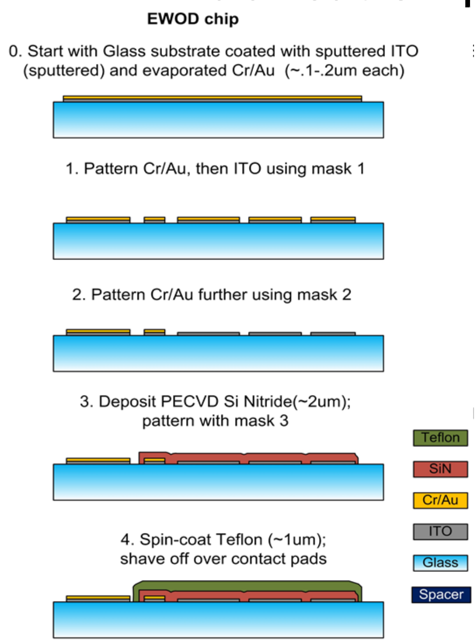
Fabrication of EWOD devices

- Most commonly fabricated in cleanroom using microfabrication techniques
- Device is built layer-by-layer:
  1. Layer is blanket-deposited
  2. Layer is patterned

Fabrication process flow

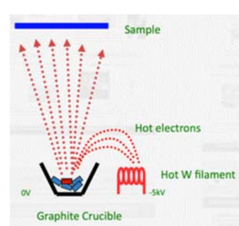


- Concise cross-sectional representation of steps of fabrication
- Details of steps are not shown, but gives an overview
- In this case, shows
  - 4 layer process
  - Materials for each layer
- Patterning is typically done using photolithography

Fab Steps: ITO and Metal deposition

Start with: Bare glass wafer coated with Indium-tin oxide (ITO): transparent but conductive layer

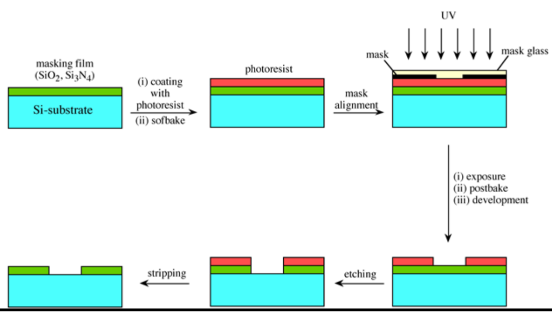
Obtained pre-deposited from large-scale supplier



E-beam evaporator: metal deposition
-Metal source bombarded with high energy electrons to evaporate metal
-Evaporated metal deposits on cooler samples, usually held in domes

Photolithography (PL)

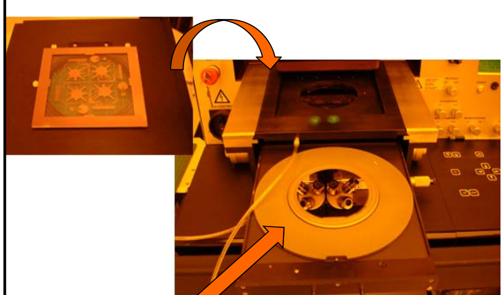
- Literally "Writing on stone using light"
- Photomask: glass plate containing precisely patterned opaque layer
  - Chromium patterned using a laser beam
- Photoresist (PR): a **photo**sensitive, chemically **resist**ant material
- Typical photolithography steps:



Photolithography with mask 1

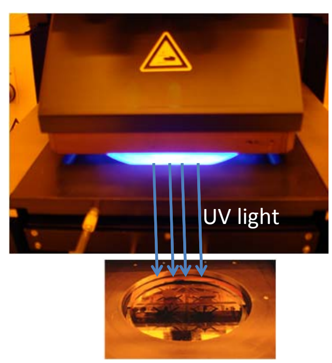
Mask 1: contains the patterns for the electrodes and contact pads

Photomask and wafer aligned on Aligner



Wafer coated with photoresist (PR)

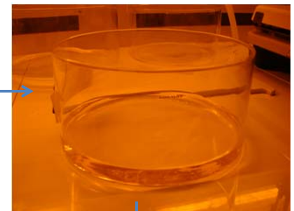
PR layer exposed through photomask



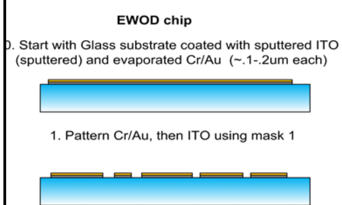
Develop and etch: mask 1

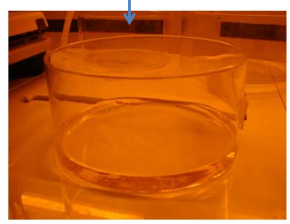
PR with mask 1 pattern after develop

Etch Au layer using PR pattern

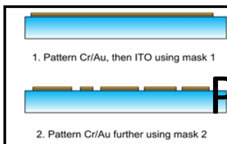


Etch Cr layer using same pattern



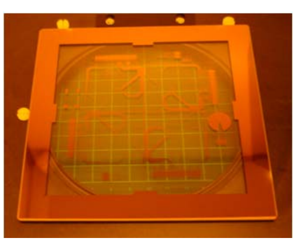


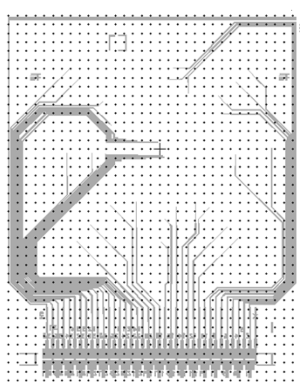
Etch ITO layer using Mask1 pattern



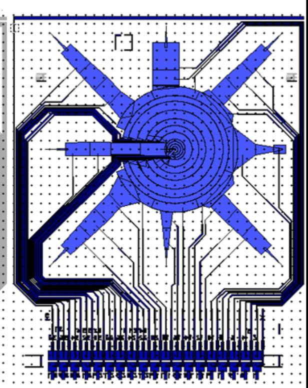
Patterning with Mask 2

- Note: Mask 2 features are a subset of mask 1
  - Only protects the contact pads and traces where Cr/Au must survive
  - Exposes the electrodes to be able to:
    - see droplet,
    - create higher resistance at the heaters





Mask 2 pattern

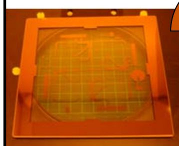


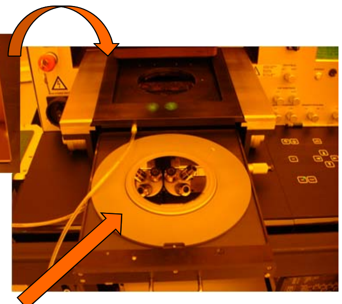
Mask 1 pattern

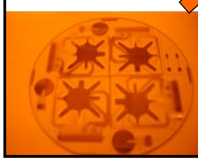
Photolithography with mask 2

Mask 2: contains the patterns for contact pads and traces
NOTE: Must align with mask 1 patterns!

Photomask and wafer aligned on Aligner

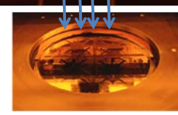




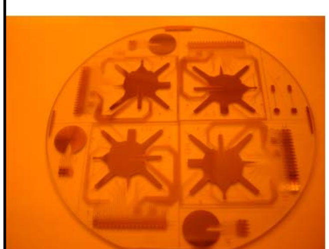


Wafer patterned with mask 2, etched and coated with new PR

PR layer exposed through photomask



Develop and etch w/ mask 2

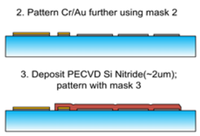


PR with mask 1 pattern after develop

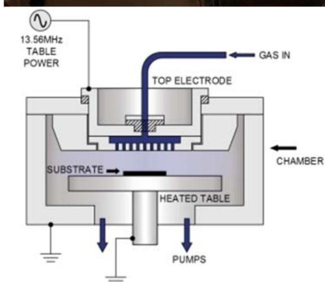
Etch Au layer using PR pattern

Similar steps as Mask 1;
-features of mask 2 are retained in Cr/Au
-

Etch Cr layer using same pattern



Dielectric deposition



- Using plasma-enhanced chemical vapor deposition (PECVD)
  - Device placed between two electrodes activated with RF voltage to create plasma
  - Gas in sealed chamber reacts on the surface to produce dielectric layer
- Silicon nitride is most commonly used by us
  - Other materials tried:
    - Silicon oxide
    - Parylene-C
    - SU-8

Considerations for dielectric material

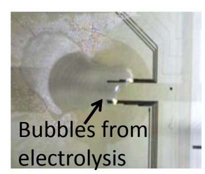
Performance considerations:

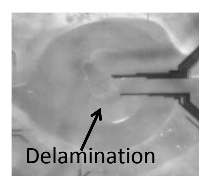
- High dielectric constant
  - Recall: EWOD force is proportional to ε_d
- High dielectric strength:
  - prevent breakdown and electrolysis-> causes damage to surface, products
- Good adhesion with substrate, metal and hydrophobic layers:
  - prevent delamination and sample loss
- Recent finding- chemical resistance may be important too!

Fabrication considerations:

- Deposition temperature
  - Au is not allowed at temperatures above ~500 degC
- Deposition time: extremely long and serial processes make fab costlier
- Repeatability of dielectric quality: above performance parameters

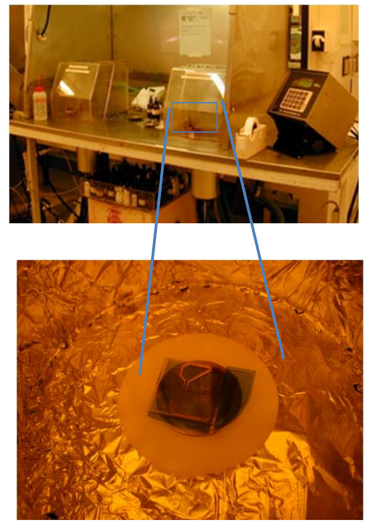
Currently looking into alternate dielectric materials, but for now, SiNx is used



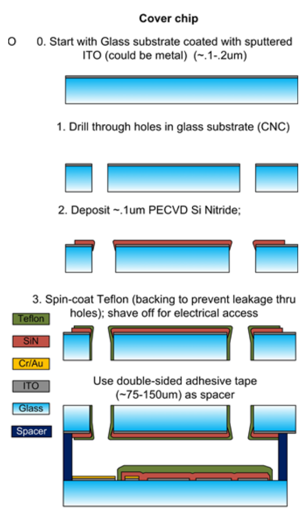


Teflon coating

- Finally, a layer of Teflon is spun-on the device
  - Hydrophobic layer to minimize the friction for droplet movement
  - Also provides (some) chemical resistance to the surface
- After spin-coating, Teflon is cured at 330 C in vacuum
- Other hydrophobic materials :
  - Cytop
  - SIOC (not available at UCLA)
  - OTS monolayers (very fragile)

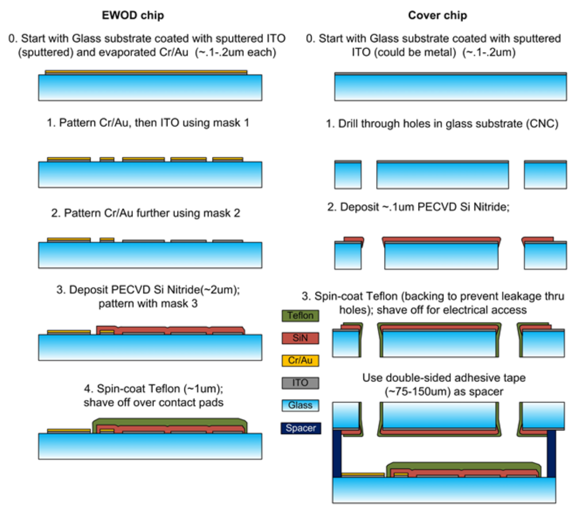


Cover and assembly



- Cover chip is much simpler and cheaper process
- Patterning is simple enough that photomasks are not needed
- Finally, chip is put together
- Spacer with known thickness is used to define gap

Summary: EWOD process flow



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- MAE 281 lecture notes on Microsciences (CJ Kim)

Outline

- Recap: background
- Electrowetting-on-dielectric theory
  - Thermodynamic: historic view, convenient 'shorthand'
  - Electromechanical : more recent, rigorous and accurate
- Device fabrication
  - Process flow and steps
  - Some key considerations
- Cleanroom tour

Thank you!
Questions before we gown up?