PHYSICS AND TECHNOLOGY OF PRINTING-BASED FABRICATION

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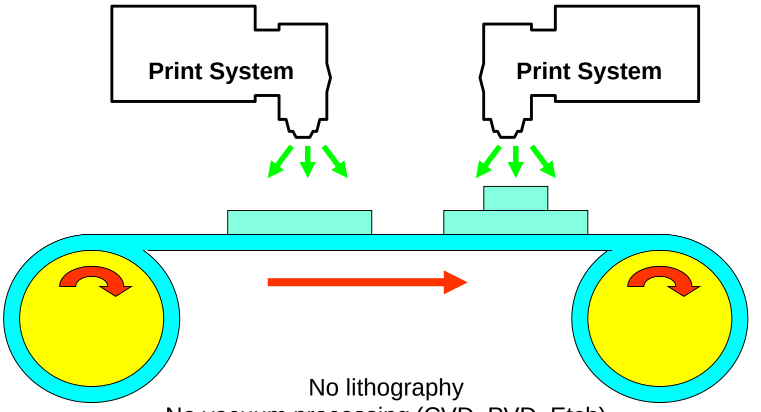
Why Print?



No lithography
No vacuum processing (CVD, PVD, Etch)
Reduced abatement costs
Cheap substrate handling
Reduced packaging costs
Net Result: cost advantage *per unit area*

Why print?

- **Low cost?**

Courtesy:
G. Cho,
Sunchon National University

- **Added functionality**
  - Integration – spatially specific deposition
  - Customizability – digital printing
  - Lightweight / robust / flexible

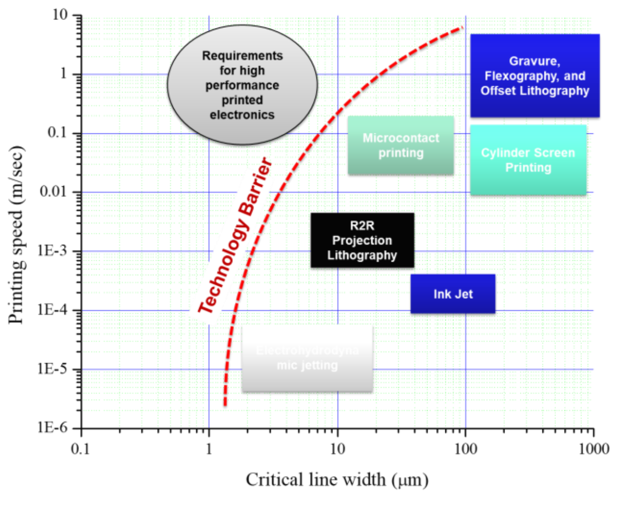
General tradeoffs in printing

- **Resolution: Printing techniques vary widely in resolution from nm (nanoimprint) to 100μm (high-speed screen)**

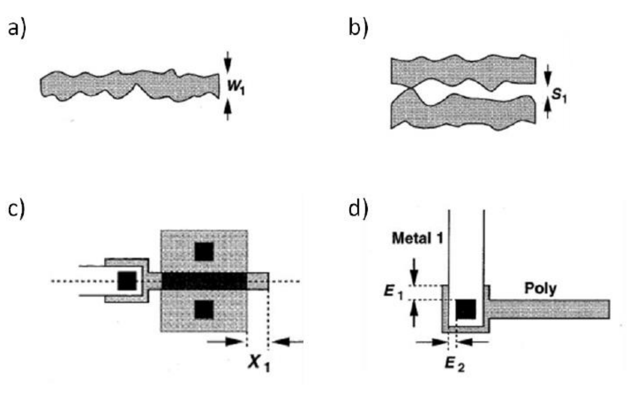
- **Speed: Traditional analog printing techniques (screen, gravure, offset) are exceedingly fast (100's of m/min), while nanoimprint is immature, and probably too slow for printed electronics**

- **Viscosity: Electronic materials often have limited viscosity ranges. Offset printing requires very high viscosity inks (like toothpaste), while digital techniques such as inkjet can work with low viscosities (e.g., alcohols)**

Resolution trade-offs in Printing



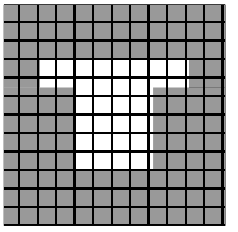
Pattern fidelity requirements

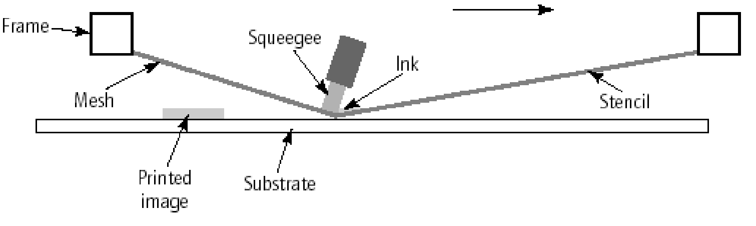


Consider:
- **Line edge roughness**
- **Line-space roughess**
- **Overlay**

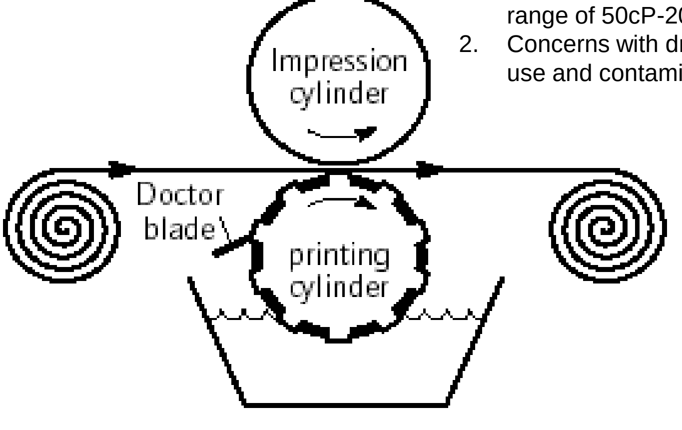
Screen Printing

Notes:
1) High viscosity is requiredto prevent bleeding
2) Resolution limits are also set by screen mesh size



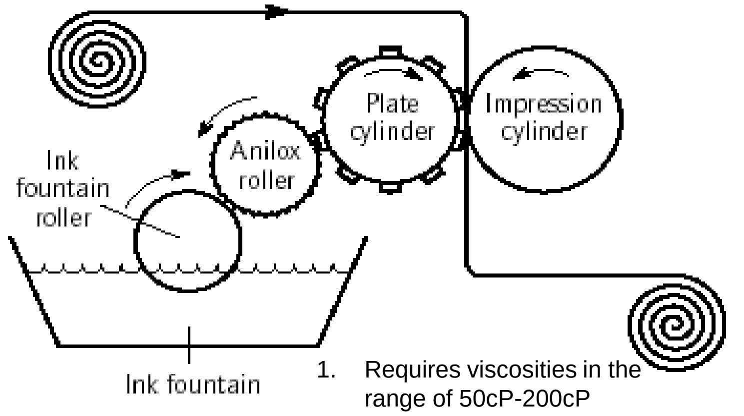


Gravure Printing



1. Requires viscosities in the range of 50cP-200cP
2. Concerns with drum re-use and contamination

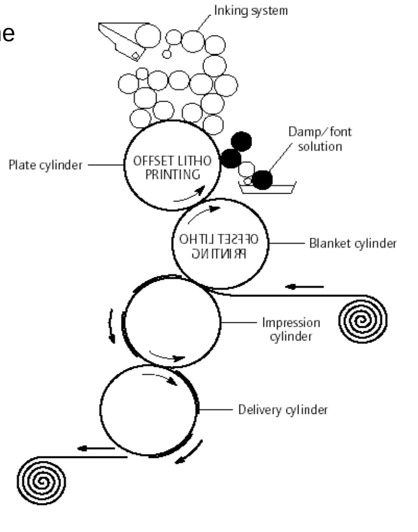
Flexographic Printing



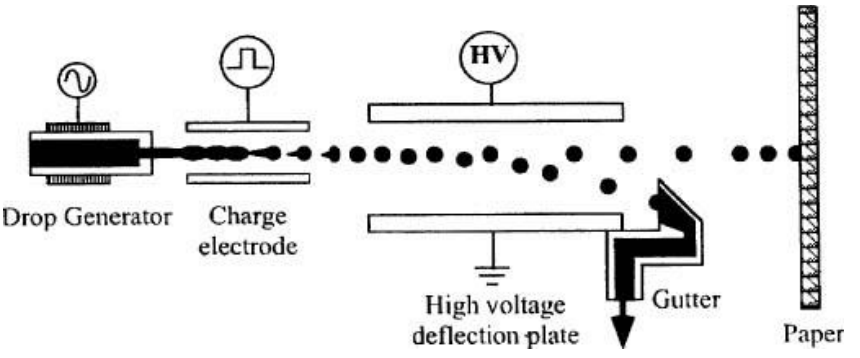
1. Requires viscosities in the range of 50cP-200cP
2. Concerns with pattern fidelity

Offset Printing

1. Requires viscosities in the range of >100cP

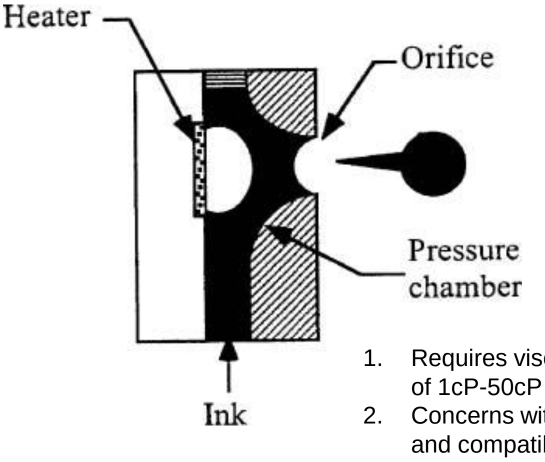


Continuous Inkjet Printing



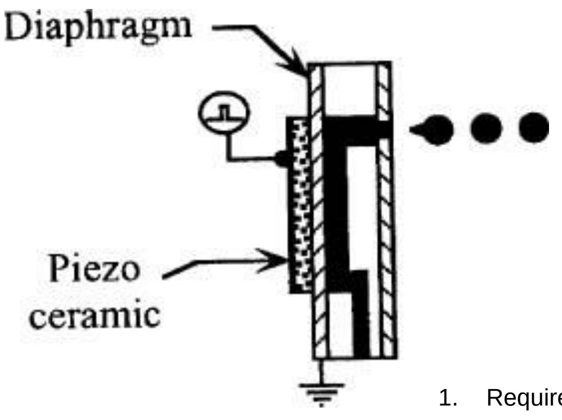
1. Requires viscosities in the range of 5cP-50cP
2. Concerns with ink wastage and contamination

Thermal Inkjet Printing



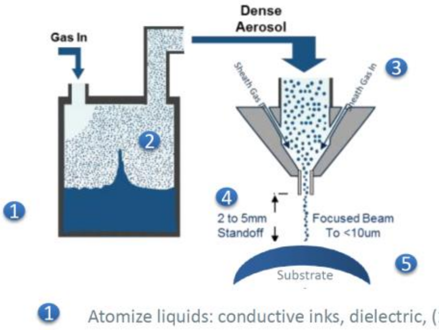
1. Requires viscosities in the range of 1cP-50cP
2. Concerns with ink degradation and compatibility

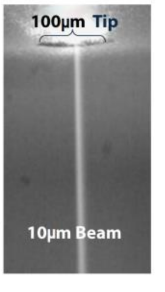
Piezo Inkjet Printing



1. Requires viscosities in the range of 1cP-50cP
2. Concerns with manufacturability

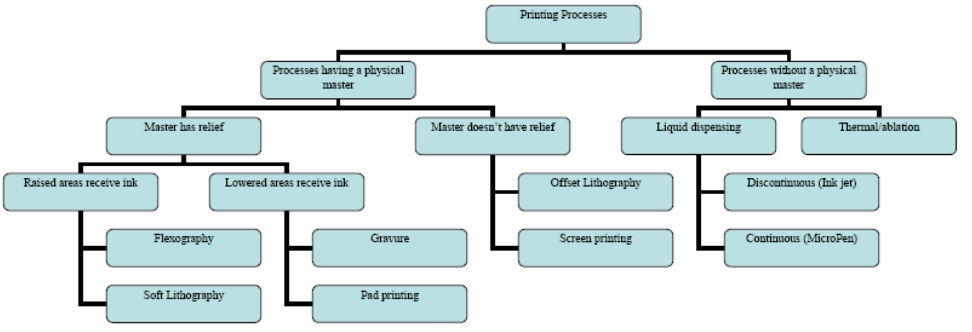
Aerosol jet





1. Atomize liquids: conductive inks, dielectric, (1-1,000 cP)
2. Mist of 1 to 5 um Ø highly dense, highly loaded droplets
3. Sheath gas surrounds and focuses particle beam
4. Continuous Flow Exits at 50m/s, remains collimated for up to 5 mm
5. Print on planar and non planar substrates

Taxonomy of printing processes

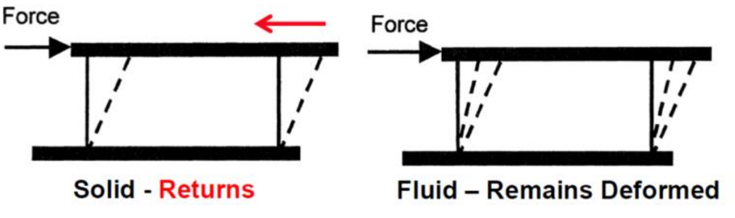


Choosing a print technique

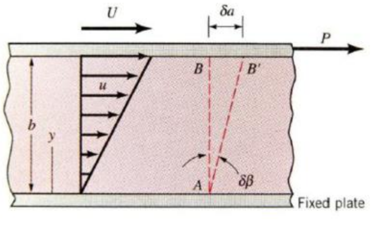
- Materials Properties
  - Viscosity
  - Surface Tension
- Physical Requirements
  - Resolution
  - Registration
  - Thickness
- Economics
  - Throughput
  - Master / Plate costs
  - Waste
  - Material Costs

What is a fluid

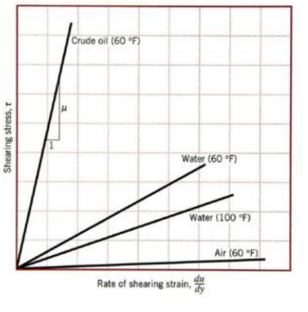
- A fluid is any substance that deforms continuously under the application of shear stress of any magnitude
- Gasses and liquids
- Newtonian liquid



Viscosity



$$\tau = \mu \frac{du}{dy}$$



where
τ is the shearing stress
μ is the absolute dynamic viscosity
$\frac{du}{dy}$ is the velocity gradient

In addition:

$$\mu \sim \mu_0 e^{-(T-T_0)}$$

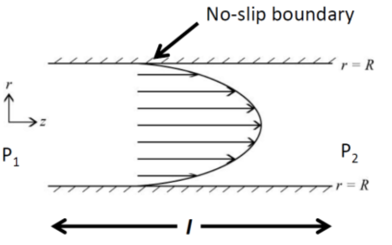
Thermal effects

Fluid flow through a pipe

Poiseuille's equation and scaling

For a fluid passing through a tube, the Naiver-stokes equation implies

$$V = \frac{\pi(P_1 - P_2)r^4}{8\mu l}$$



For narrow pipes the flow rate (V) is strongly reduced.

Household pipes
ΔP=3 bar, R=5 cm
μ= 0.01 poise, L = 10m
V= 73 m/s

Washing machine
ΔP=3 bar, R=1 cm
μ= 0.01 poise, L = 5 m
V= 0.2 m/s

Ink-jet printer
ΔP=3 bar, R=100 μm
μ= 0.01 poise, L = 5 cm
V= 20 μm/s

The Reynolds number

- The Reynolds number is a ratio between the internal forces in a fluid and the viscous forces

$$Re = \frac{\rho V D}{\mu}$$

Where
ρ is the fluid density
V is the fluid velocity
D is the pipe diameter
μ is the viscosity

Re < 2100
- Laminar (Stokes) flow
- Slow fluid flow
- No inertial effects
- Heavy damping

Re > 4000
- Unstable laminar flow
- Turbulent flow

Osborne Reynolds
Born Belfast 1842
First UK "Professor of Engineering"

The Reynolds number in inkjet printing

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V= 20 μm/s

Water density = 10^3 kg.m^3
Viscosity = 10^{-3} kg.s^{-1}.m^{-1}

Re=3.65 x 10^6

Re=2000

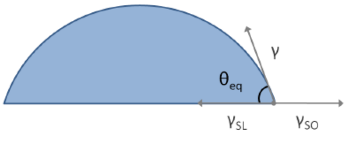
Re=2 x 10^{-4}

- For most flow rates and small pipes Re is small and the flow is laminar
- Viscosity is dominant and we are in the realm of Microfluidics!

Liquids on surfaces: Some basic discussion

$$\gamma \cos \theta_{eq} = \gamma_{SL} - \gamma_{S0} \quad (1)$$

The fluid's surface tension is γ, and γ_{SL} and γ_{S0} represent the substrate-liquid and substrate-air interfacial tensions, respectively.



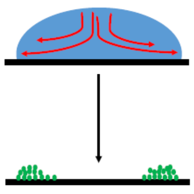
The substrates in this work are rough and have defects, and the printed inks dry and deposit solute. For both of these reasons, the contact line's advancing (θ_{adv}) and receding (θ_{rec}) contact angle separate in value leading to contact-angle hysteresis. The contact line is stable when $\theta_{rec} < \theta < \theta_{adv}$, else it retreats or advances as appropriate. Evaporating colloidal inks often have zero retreating contact angle and are said to have pinned contact lines that may advance but never retreat.

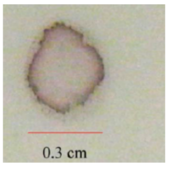
Effects with real inks

"Coffee Ring" Effect and Marangoni Flow

- During solution evaporation, there are two major competing evaporation-driven effects, "coffee ring" effect and Marangoni flow.

"Coffee ring" Effect

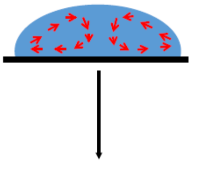


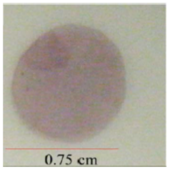


Au NP pattern induced by "coffee ring" effect

Dense, ring-like structure along the perimeter
1) Absence of circulating flow
2) Contact line of drying droplet is pinned
3) Outward flow carries solutes to the periphery

Marangoni Flow



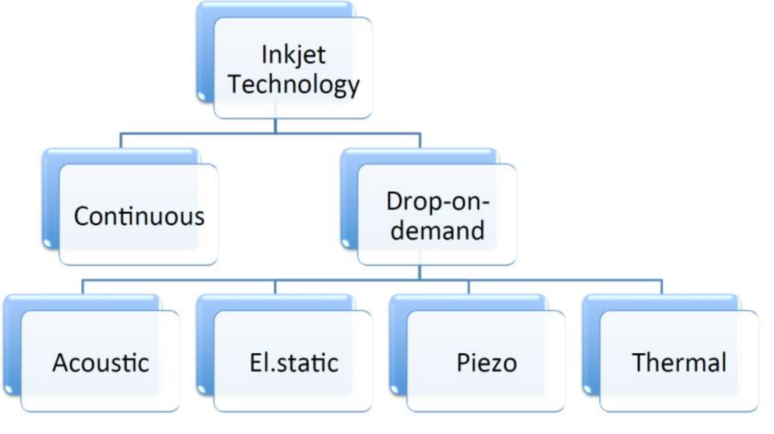


Au NP pattern induced by Marangoni flow

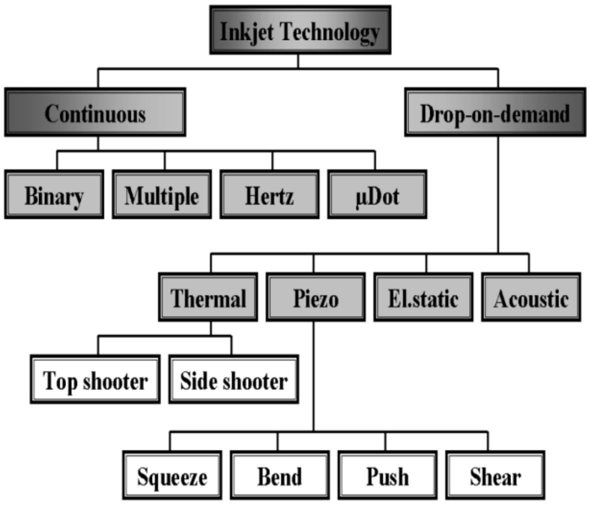
Ordered structure across the surface

The surface tension driven flow carries particles inward toward the top of the droplet and then plunges them downward where they can either adsorb onto the substrate near the center of the droplet or be carried along the substrate to the edge, where they are re-circulated along the free surface back toward the top of the droplet.

Taxonomy of major inkjet technologies

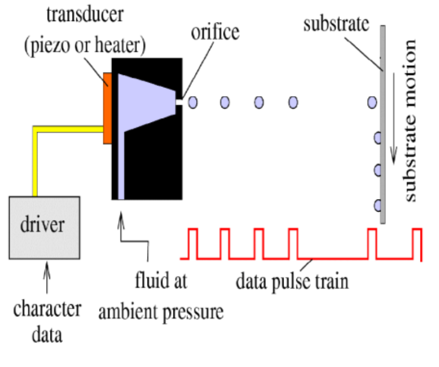


Drop formation mechanisms



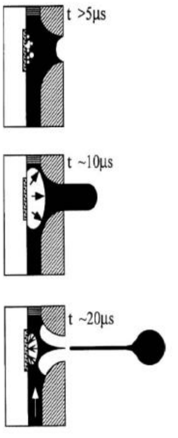
Droplets on demand inkjet printing

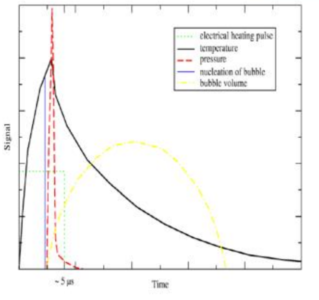
- Mechanism of droplet formation:
  - Thermal
  - Piezo-electric
  - Electrostatic
  - Acoustic

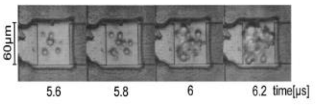


Thermal inkjet printing

- Phase of droplet formation
- Heating
  - Overheated ink (over the spinodal limit, around 300°C for water)
  - At 300°C: nucleation of bubble
- Expansion
  - Ejection of ink
  - Parallel to bubble expansion
- Droplet formation
  - Collapsing vapour bubble
  - Retraction of bulk ink
  - Refilling of cavity (80-200 us, speed critical step)

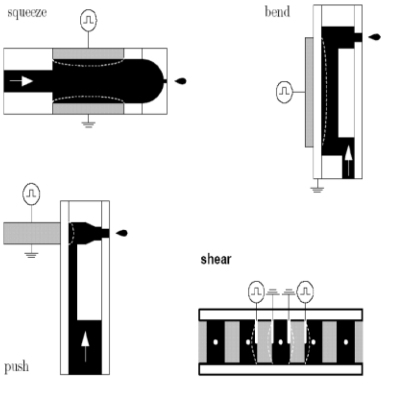






Piezo inkjet printing

- Deformation of piezo-ceramics
- Change in volume
- Pressure wave propagates to nozzle
- Deflection of piezo-ceramics in submicrometric range
- Piezo-element has to be much larger than orifice
- Main problem: miniaturization



Droplet formation in piezoelectric inkjet printers

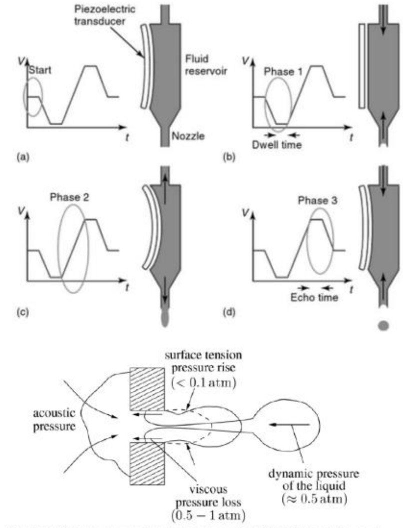
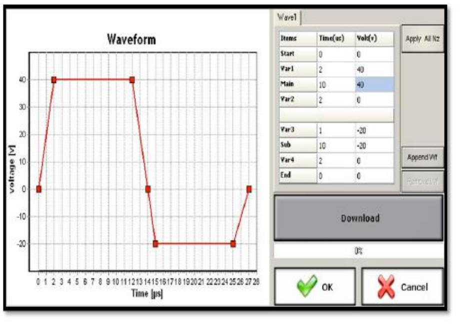


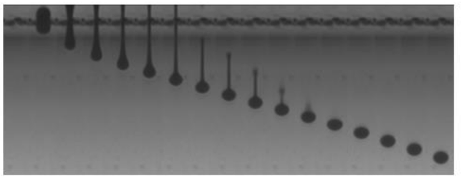
Fig. 8.5. Pressures governing the ejection dynamics of a liquid jet out of a nozzle

a) Starting deflection
b) Ink influx & meniscus formation
c) Acoustic -> kinetic energy
   high velocity jet from nozzle
   - Viscous pressure loss
   - Negative pressure wave reflection
   - Drop formation

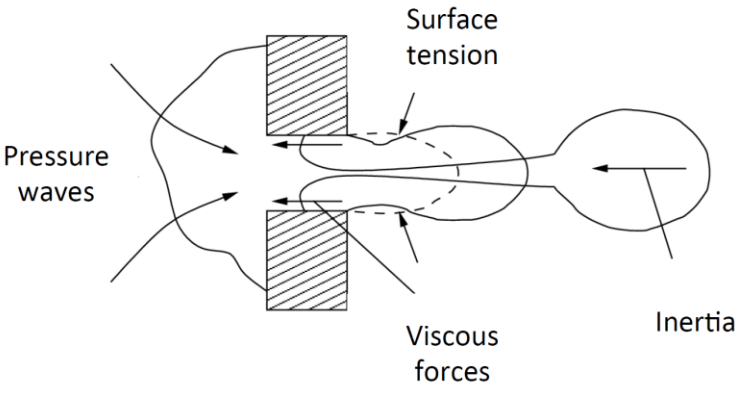
d) Cavity relaxation period & meniscus formation

Example: typical bipolar waveform





Ink design considerations



Ink formulation

The weber number relates the balance between inertial and capillary forces in a fluid

$$We = \frac{\rho V^2 D}{\gamma}$$

Where
ρ is the fluid density
V is the fluid velocity
D is the pipe diameter
γ is the surface tension

The Ohnesorge number is the ratio of the Reynolds and Webber numbers

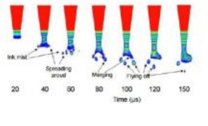
$$Oh = \frac{We^{1/2}}{Re}$$

Inverse ratio gives the Z index for inks

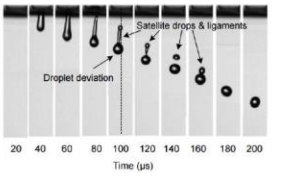
$$Z = Oh^{-1} = \frac{(D\rho\gamma)^{1/2}}{\mu}$$

Numerical criteria for ink formulation

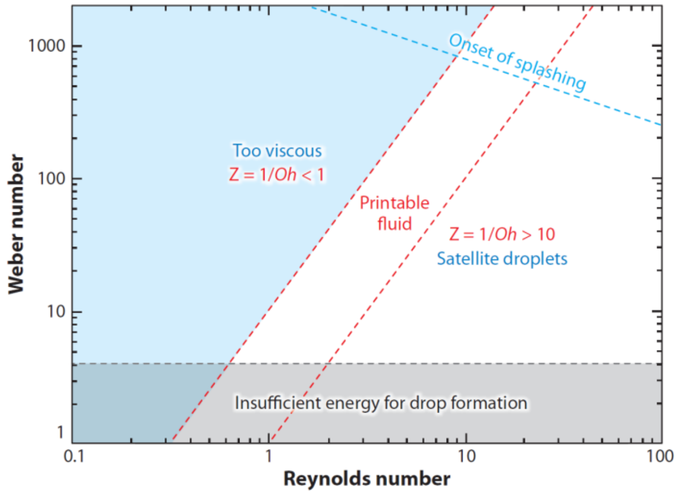
Z > 2 for successful printing
Viscosity large enough to dissipate acoustic-> kinetic shock



Z < 70
Satellite Droplets form separately to the main drop

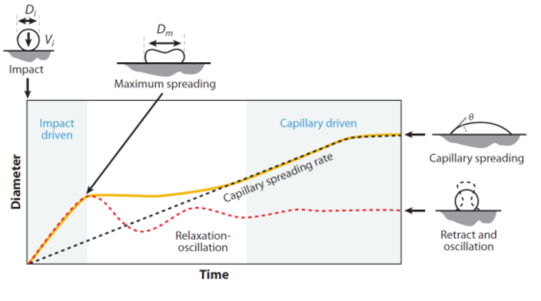


Drop ejection



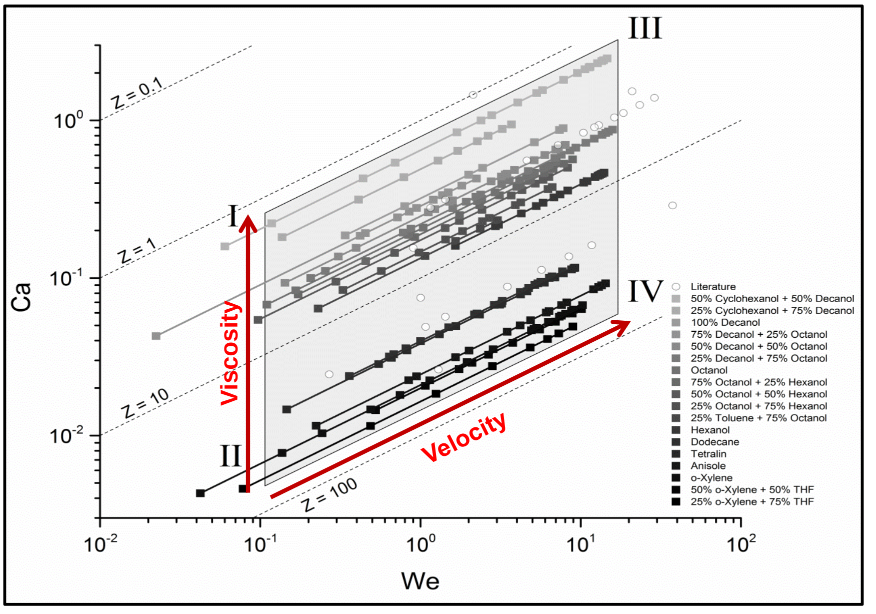
On the surface

Physics of drop: impact

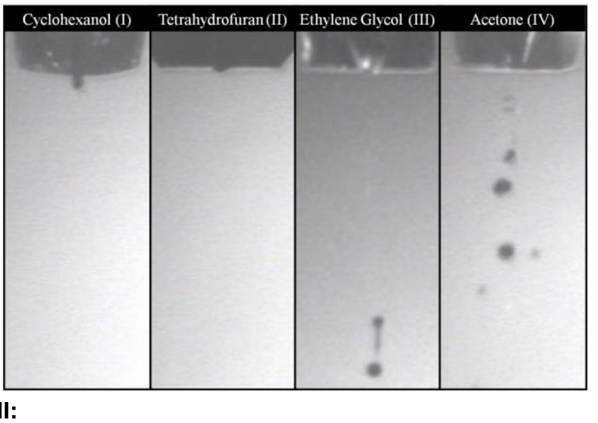


- The final diameters is a linear function D_i
- The drop footprint increases with decreasing the contact angle and is about $3D_i$ at a contact angle of 10°
- Coffee ring effect

Jettability Window



Breakdown Mechanisms Observed

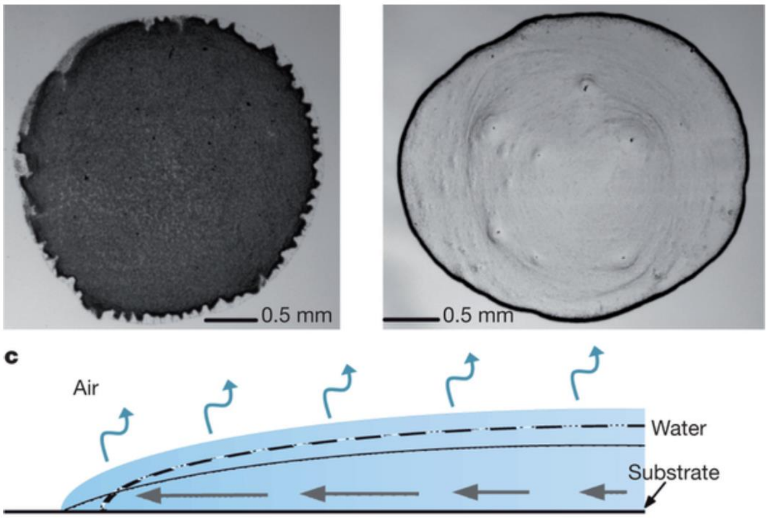


Regions I and II:
- **intertial force (driven by pulse amplitude) too low for drop ejection**

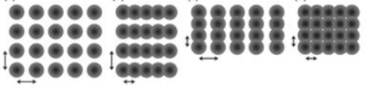
Region III:
- **emerging ink pillar too long → satellite drops form from tail of drop**

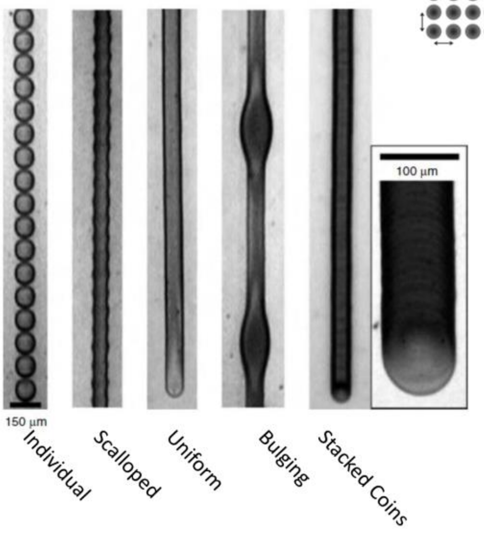
Revion IV:
- **inviscid ink subjected to large intertial force → wavelike instability created → multiple breakups of drop tail**

Reminder: the coffee ring effect



Pattern formation





- Patterns of dots
- Dot spacing

Wetting

$$\gamma \cos(\theta_{eq}) = \gamma_{SL} - \gamma_{LG}$$

Drying effects

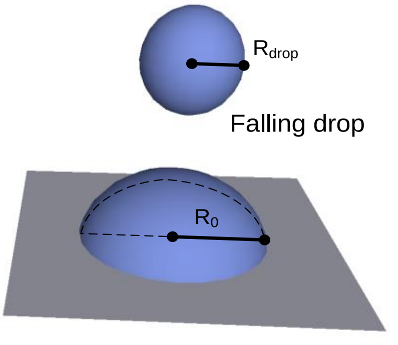
Substrate choice

γ_{ink} < Substrate surface energy

- Coating
- Functionalizing

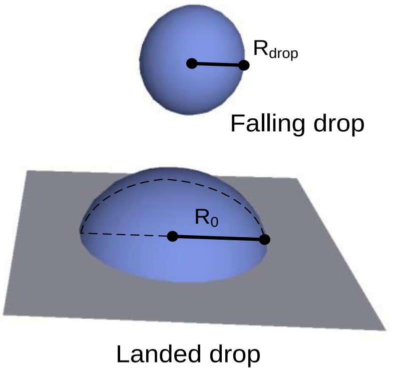
So what causes these effects?

- **Step 1: Drop hits the surface and expands to an impinging radius Ro**



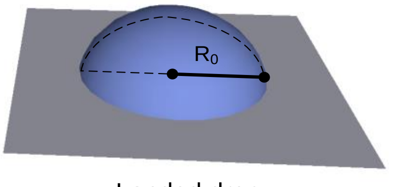
So what causes these effects?

- **Step 2: Edge of drop is “pinned”**

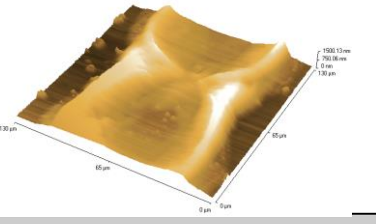


So what causes these effects?

- **Step 3: In isolated drops, drying causes:**
  - **Convective flow: edge is cooler than center, causing outward flow of material (coffee ring effect)**
  - **Marangoni effect: surface tension is temperature dependent, causing flow of material (can reverse coffee ring effect).**
  - **Final structure depends on relative rates**

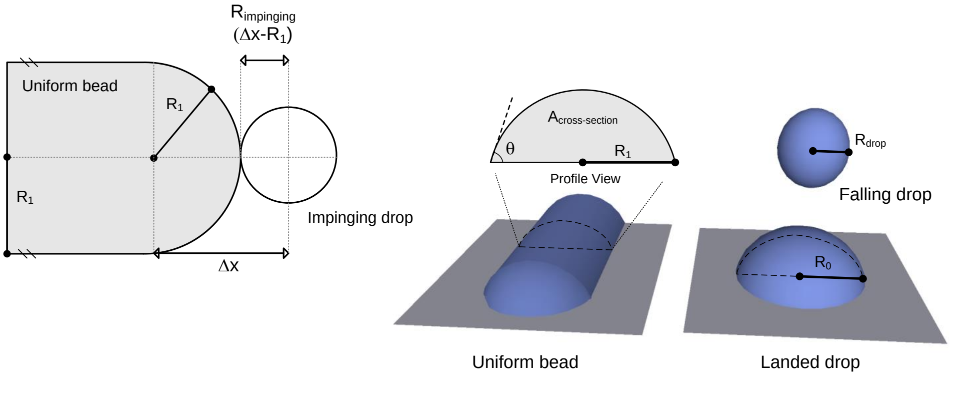


Landed drop



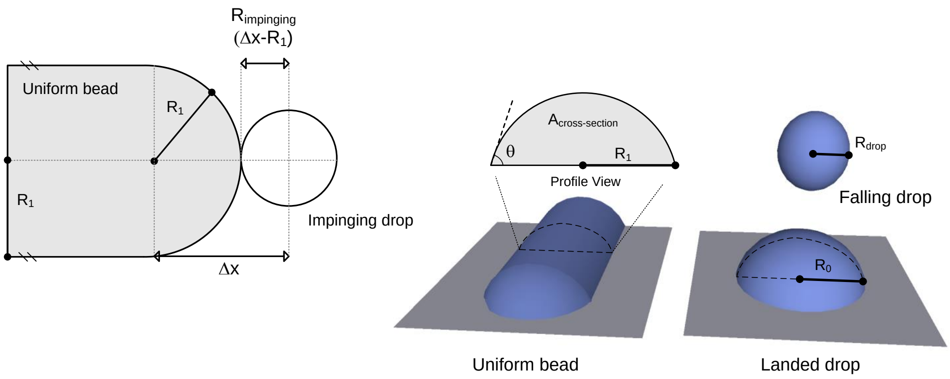
What happens in lines?

- **Step 1: Impinging drop “connects” to bead of line, and material flows back into line for same reason that coffee ring occurs**



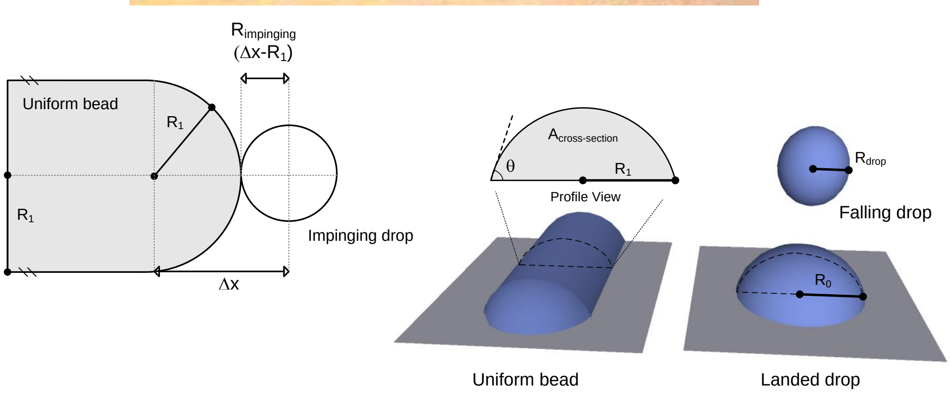
What happens in lines?

- **If flow is too slow, drop "dries" before line evens out, causing scalloping**

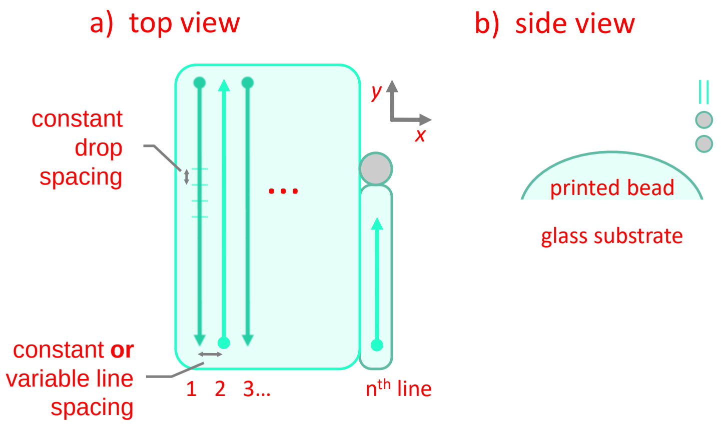


What happens in lines?

- **If flow is too fast, bead cannot absorb material fast enough, causing bulging**



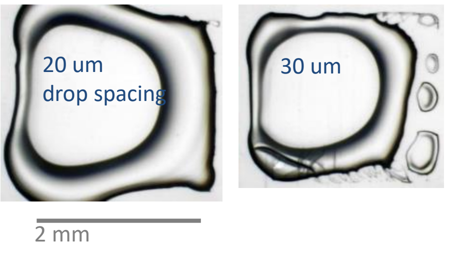
Two dimensional shape generation

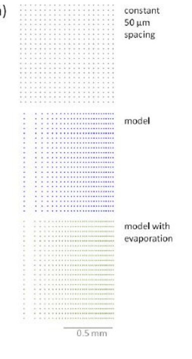


- **As patterns are printed, the contact angle of the bead can go in and out of the steady-state zone… this leads to instabilities**

Bulging and instability in two dimensions

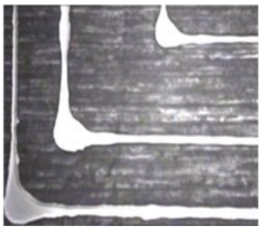
- **Dense drops cause bulging**
- **Sparse drops cause bead separation (since bead contact angle drops below receding contact angle)**

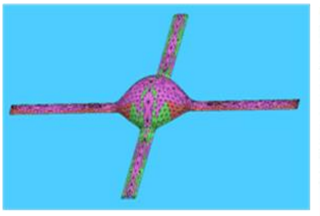


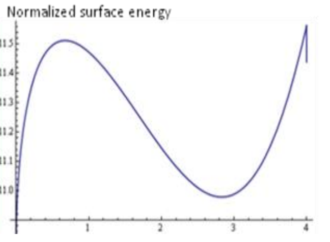


- **There is therefore an inherent limit to constant-space printing, which is what *all* existing tools tend to do.**
- **Solution: adjust drop spacing to control stability**

Instabilities in corners





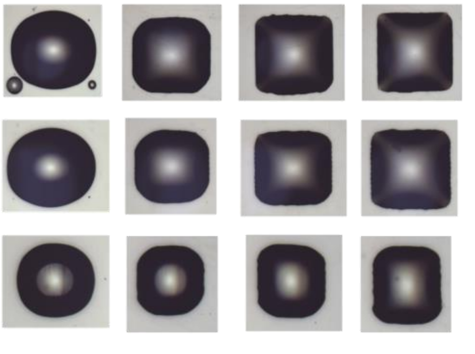


- **Flow in corners can drive to formation of bulges**
  - **Can position to equilibrium that eliminates bulges by proper design of process**
  - **Can exploit bulge formation to cause linewidth shrinking… (more on this later)**

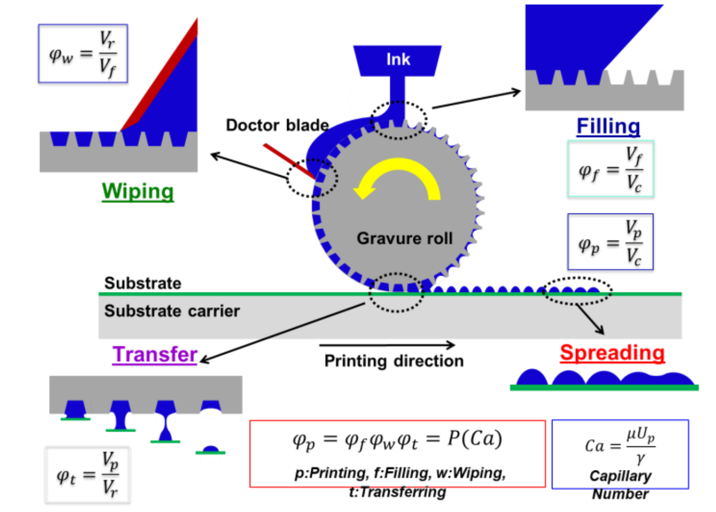
The impact of the substrate

- **E.g., controlled contact angle hysteresis**

Increasing hysteresis (fixed θ_A, decreasing θ_S

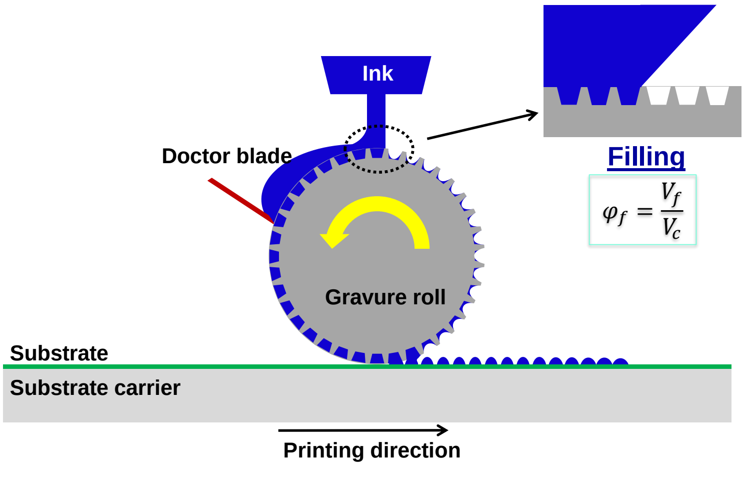


Gravure Printing

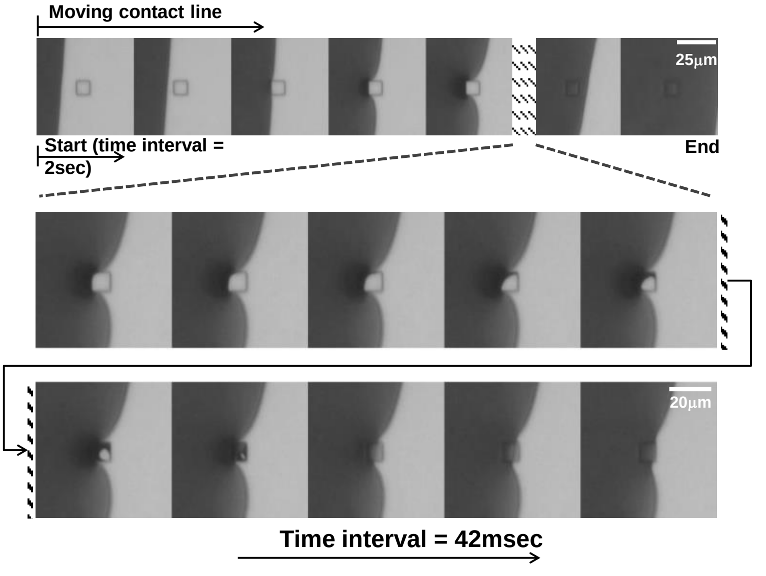


Kitsomboonloha, R., Morris, S. J. S., Rong, X., & Subramanian, V. (2012) *Langmuir*, *28*(48), 16711–23

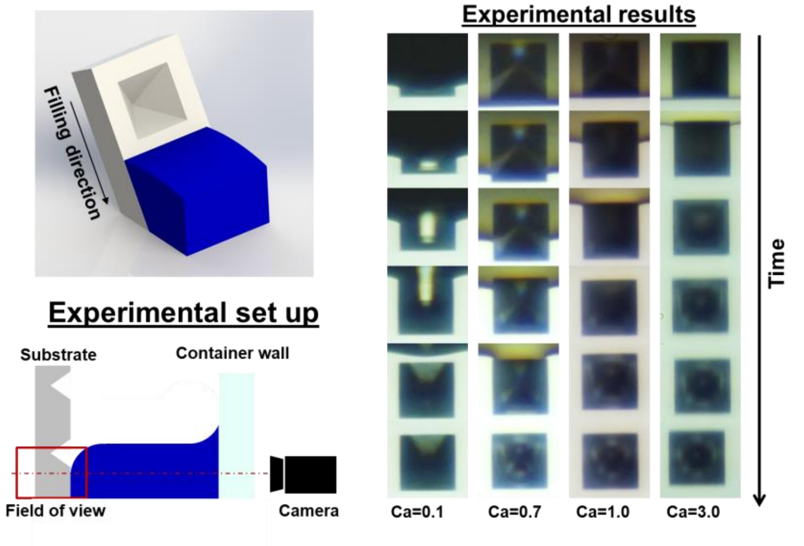
Filling Process



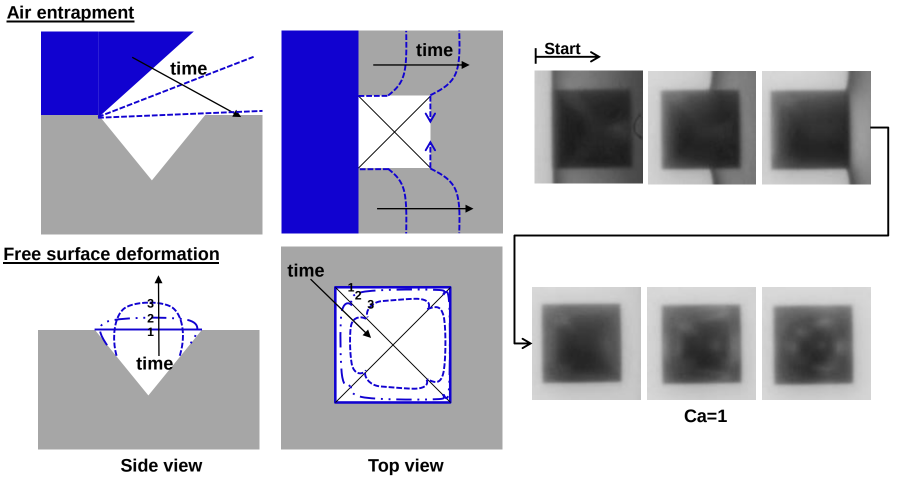
Filling Mechanism



Filling Mechanism

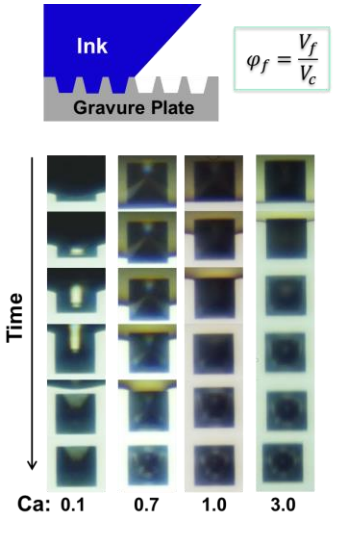


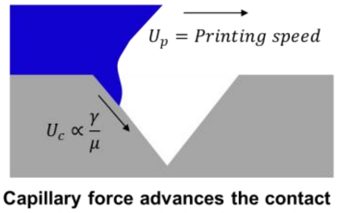
Air entrapment



Assume prefect pinning at the cell edges

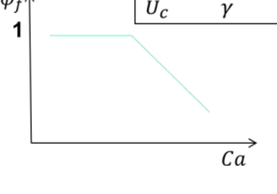
Filled Volume Fraction





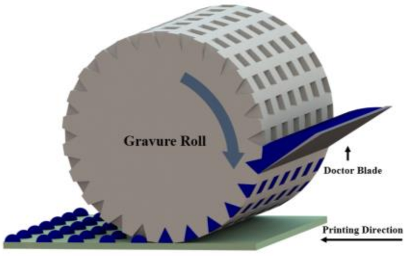
Capillary force advances the contact line advances with the characteristic velocity.*

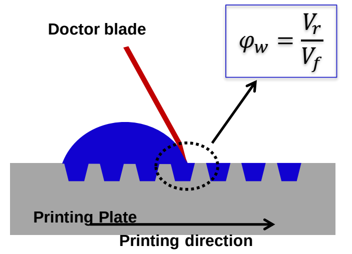
$$\frac{U_p}{U_c} = \frac{\mu U_p}{\gamma} = Ca$$

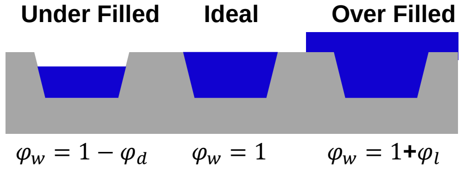


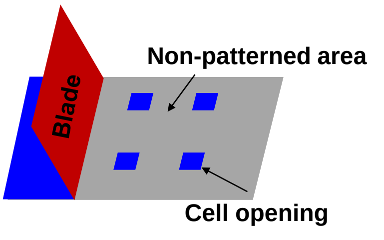
* Gennes, P. D.; Brochard-Wyart, F.; Quere, D. ,Springer, 2004.

Wiping Process





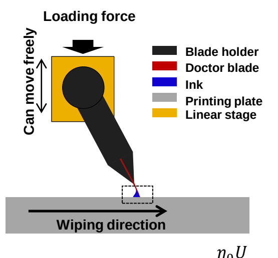




φ_d = Drag-out volume fraction

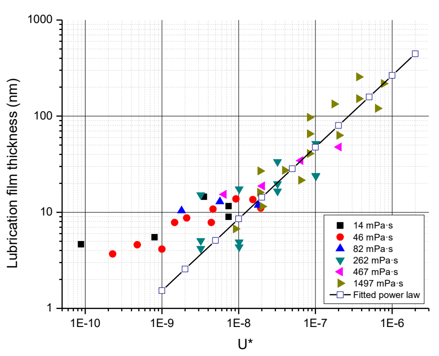
φ_l = Lubrication film volume fraction

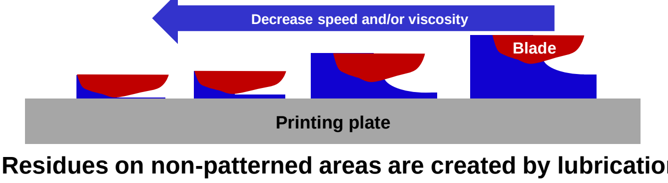
Wiping on Non-patterned Areas



Dimensionless speed: $U^* = \frac{\eta_0 U}{E'R}$

For our system, Ca=1E8×U*

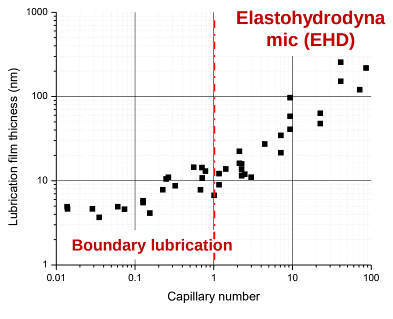




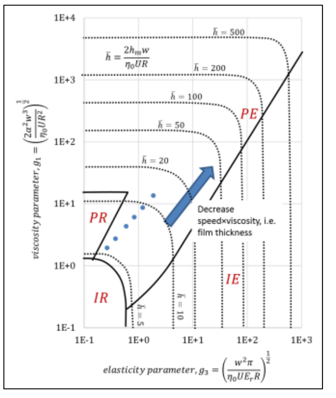
Residues on non-patterned areas are created by lubrication films between the blade and printing plate.

Lubrication Films in Gravure

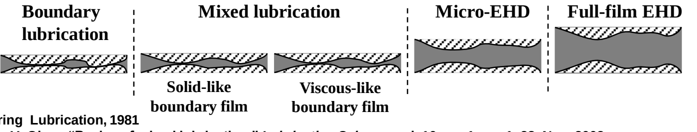
Film thickness[1]: $h \propto U\eta^{0.67}$



Lubrication regimes[3]:



Regions of EHD lubrication films[2] :

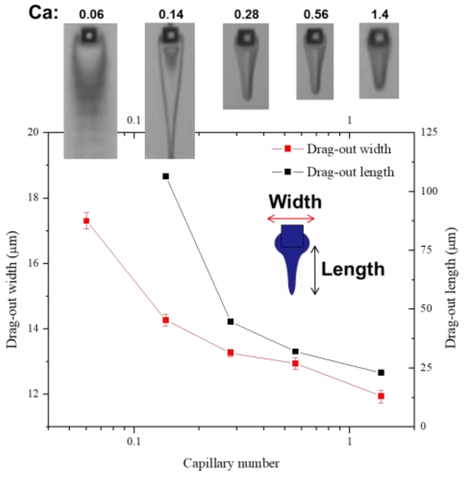


[1]Dowson, Ball Bearing Lubrication, 1981

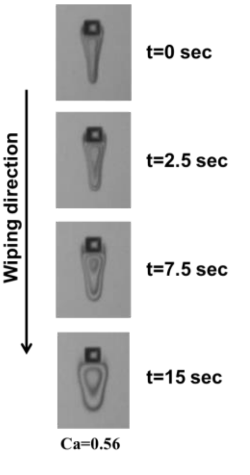
[2]H. A. Spikes and A. V. Olver, "Basics of mixed lubrication," *Lubrication Science*, vol. 16, no. 1, pp. 1–28, Nov. 2003.

[3]Johnson, K. L. , "Regimes of elastohydrodynamic lubrication", *Journal of Mechanical Engineering Science 12*(1), 9–16, 1970.

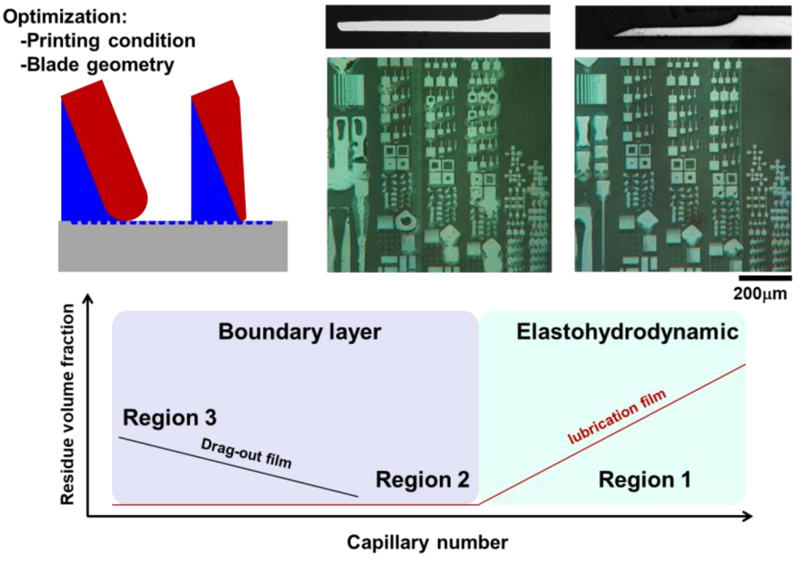
Characteristic of Drag-out Tails



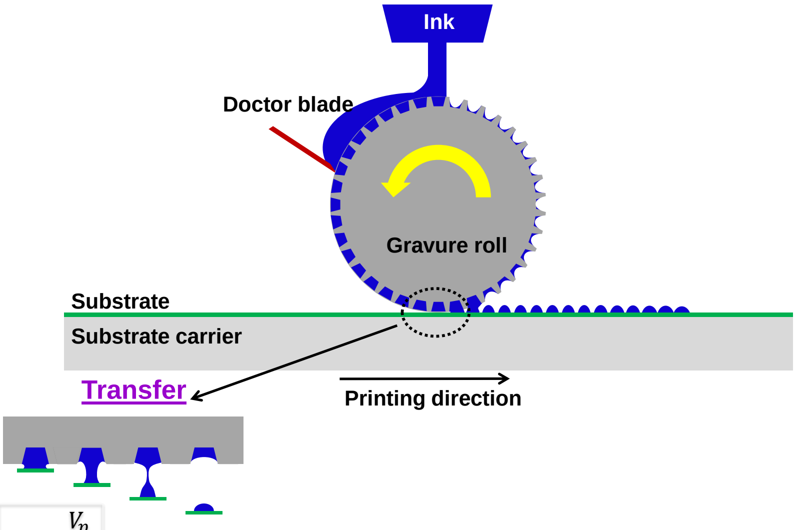
After released from doctor blade



Perfect Wiping

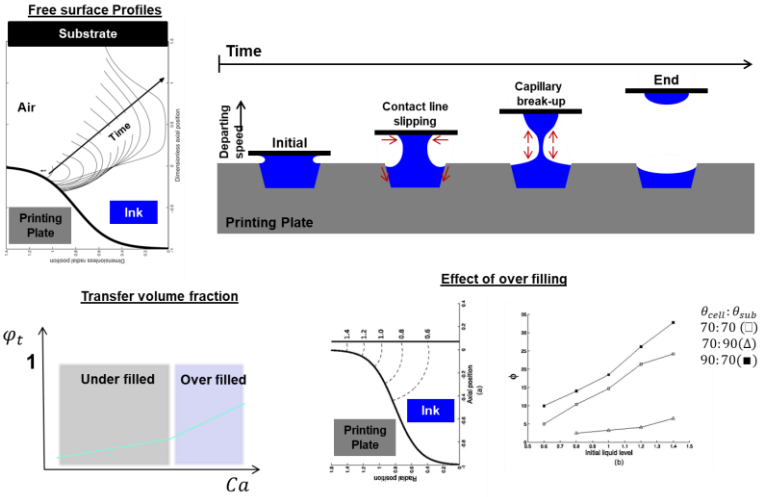


Transferring Process



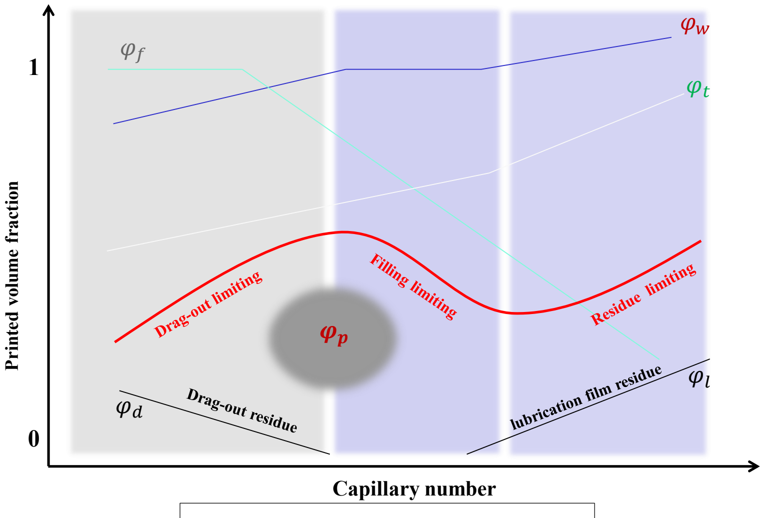
$$\varphi_t = \frac{V_p}{V_r}$$

Transfer Mechanism



Shawn Dodds, Marcio da Silveira Carvalho, and Satish Kumar *Physics of Fluids* 21, no. 9 (2009): 092103

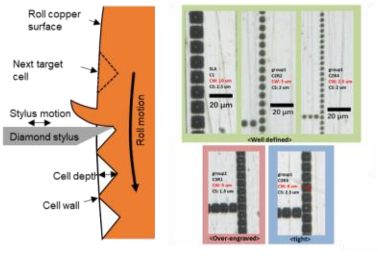
Characteristic of Gravure Printing



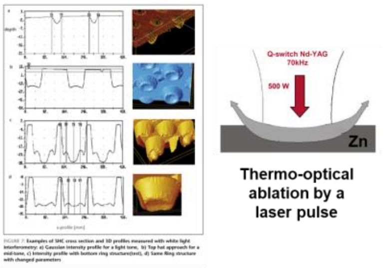
Printed volume fraction: $\varphi_p = \varphi_f \varphi_w \varphi_t$

Current Roll Engraving Technology

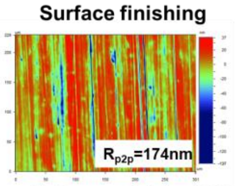
Electromechanical (EM)



Direct Laser (DLS)*



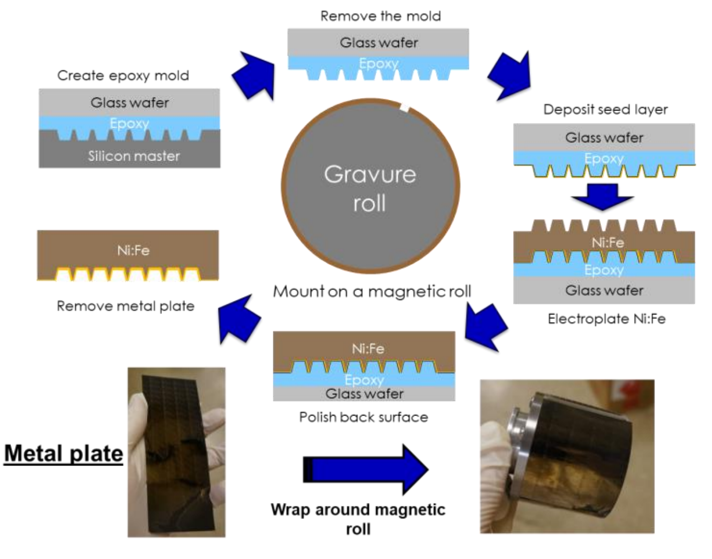
Surface finishing



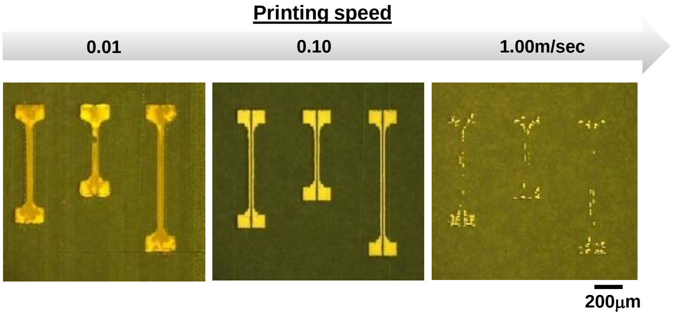
Limitations:
1) Minimum cell size
2) Incorporate various cell sizes closely
3) Surface roughness

*Hennig, G (2005). Laser engraving in gravure industry, doi:10.1117/12.660938

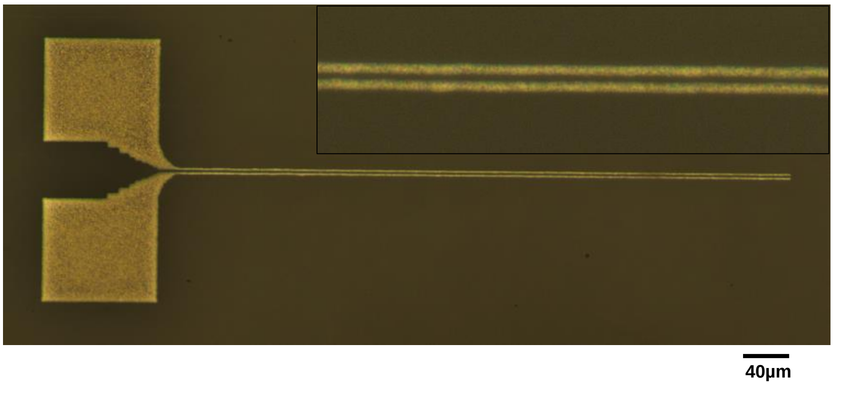
High-Resolution Roll Fabrication



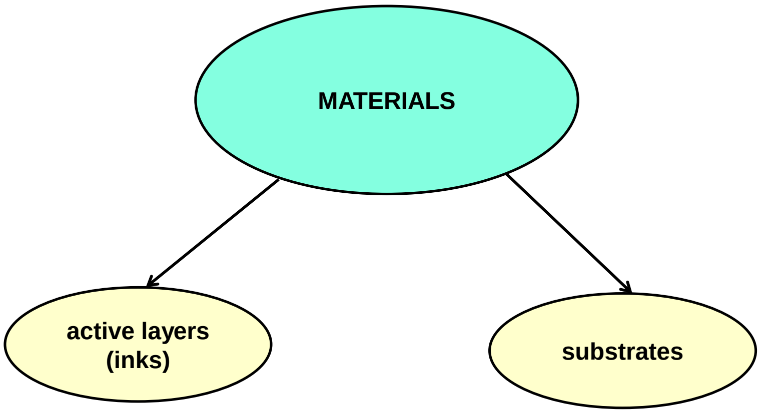
Printed Volume Fraction



<2μm Printed Channel



Materials for printing-based manufactoring



Inks for functional printing-based manufacturing

Characteristics of an ideal ink:

1) easy to print and cure;
2) able to achieve the maximum resolution allowed by the specific printing technique;
3) chemically compatible with the highest possible number of substrates and with other inks (in case of multilayered printing);
4) should have the best possible functional characteristics it was designed for (for instance: a conductive ink should provide good electrical conductivity of the printed pattern);
5) should cause minimum printing equipment maintenance.

In order to be deposited, the physical characteristics of an ink have to be carefully tuned according to the chosen deposition technique:

1) viscosity;
2) surface tension*;

***Electrically conductive inks for inkjet printing*. MM Nir et al. (World Scientific, 2010)**

Inks for large area manufacturing

Printing technique	Required viscosity [cP]
Screen printing	500 – 50,000
Flexography	50 – 500
Gravure	50 – 500
Offset lithography	40,000 – 100,000
Inkjet printing	1 - 30

Roughly speaking:

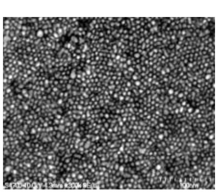
- techniques in which the ink is subjected to high mechanical stress require high viscosity inks;
- high viscosity inks usually tend to form thicker layers.

Adapted from *Organic Electronics: Materials, Manufacturing and Applications*, H. Klauk, (Wiley VCH, 2006) ISBN: 3527312641

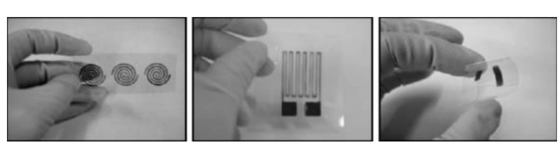
Inks for printed conductors

Conductive inks:

- **inorganic: metallic NPs (Au, Cu, Ag) based inks;**
- **organic carbon based inks: carbon black;**
- **organic polymeric inks: PEDOT:PSS, PANI;**
- **experimental: CNT inks, graphene inks.**



Ag NPs ink (TEM image)



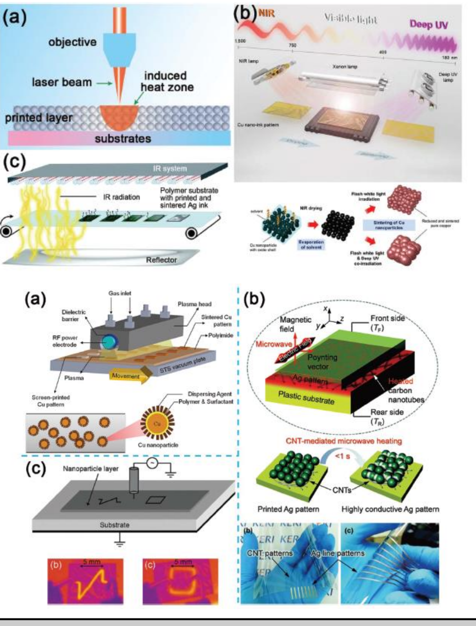
Inks curing

Curing is a process necessary to remove the solvents (i.e. the "liquid part") from the ink and also to improve/stabilise its physical properties.

Curing may be performed using different techniques, the choice essentially depends on the specific ink or substrate chosen:

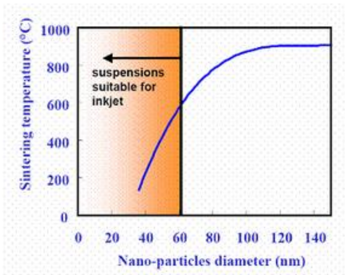
1. **Physical drying:** the solvent evaporates from the ink, only the solid content remains on the substrate. This process requires thermal energy, it can be performed in an oven, on a hotplate, with laser, microwaves…
2. **UV curing:** the ink is irradiated with UV light, which initiates the formation of free radicals responsible for the polymerisation of molecules.
3. **Chemical curing:** the polymerisation/cross-linking are induced by chemical reactions. Some of them may occur at room temperature but, in general, this process is sped up by thermal energy.

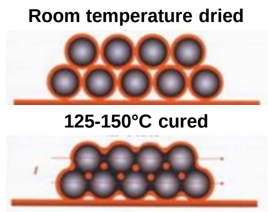
Overview of non-thermal sintering approaches

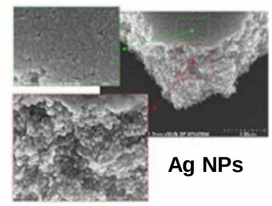


Inks curing: sintering

For nanoparticles-based inks for printing

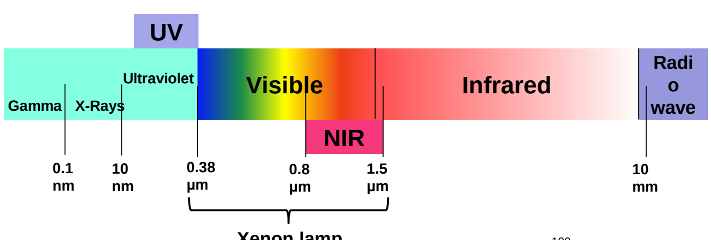






- When the particles are printed and dried at room temperature they are electrically insulated from each other by their polymeric shells
- Low temperature (125C) curing allows the shells to flow and the nanoparticles to come into electrical contact with each other.
- Once the polymer shells have reflowed an electrically continuous percolation network is formed that is conducting.
- Increasing the curing temperature from 125C to 250C decreases the resistivity and further volatizes the polymer shell, which is eventually eliminated.

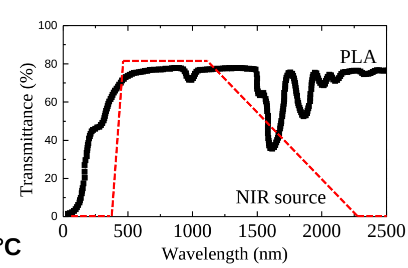
Inks curing: photonic sintering



Novacentrix

Photonic flash sintering (Xenon lamp)

- 200 – 1500 nm
- Duration controlled by pulses (µsec)
- Energy: 3000-5000 mJ/cm^2
- Absorption of metal much higher than substrate: Substrate remains at low T°C
- Reduction of CuO to print Copper
- High throughput (100m/min) i.e. R2R



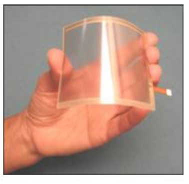
W. Mulbry et al. Bioresource Tech. 109 (2012), 93-97.
C. Aulin et al. Appl. Mater. Interfaces 2013, 5, 7352-7359.
A. Ulrici et al. Chem. Intelligent Lab. Sys. 122 (2013), 31-39.

Substrates for large area manufacturing

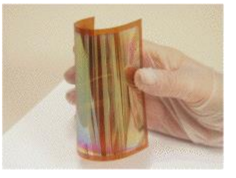
<u>Definition</u>: any base (surface or material) on which the active pattern is finally reproduced.

Crucial aspect: <u>optimum match between</u> the ink and the substrate!

1) **ink drying and curing → chemical compatibility, substrate resistance to curing;**
2) **good adhesion between ink and substrate → requirements in terms of roughness, porosity and polarity.**



***Organic Electronics: Materials, Manufacturing and Applications*, H. Klauk, (Wiley VCH, 2006) ISBN: 3527312641**



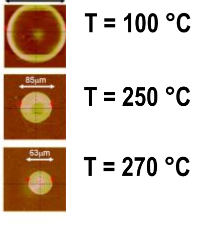
Substrate modification

Sometimes, to make a substrate more suitable for a specific deposition process, it is necessary to treat its surface in order to modify its physical/chemical properties.

1) <u>Substrate heating</u>

This method increases the velocity of solvent evaporation. Its main effects are:

- improve printing resolution (the drop dries before it has time to spread);
- increase the thickness of deposited layers (possibility to deposit one layer on the top of another one).



Drawbacks:

- not all printing technologies allow to heat the substrate;
- substrate temperature must be carefully controlled in order to avoid damage to the substrate, the printed layer and the printing equipment.

***Laser based hybrid inkjet printing of nanoink for flexible electronics*, Ko et al., Proc. SPIE 5713, 97 (2005)**

Substrate modification

2) Hydrophobic/hydrophilic modifications:

In order to insure good adhesion between ink and substrate, they must have the same "affinity for water".

Hydrophobic substrates are usually indicated for oily, non-polar inks while hydrophilic substrates are more compatible with water based inks.

What if we want to print a non-polar ink on a hydrophilic substrate or vice versa?
The substrate surface properties must be modified.

Surface chemical or physical modification can help also for the adhesion of the layers

Treatments to modify the substrate surface affinity:

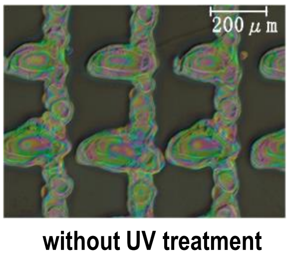
1) UV exposure, plasma treatment or corona discharge (usually used to increase the hydrophilicity);
2) Deposition of adhesion layers on the substrate.

Substrate modification

3) Plasma/UV treatment:

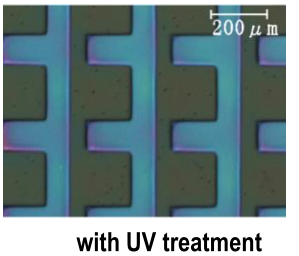
Such high energy treatments modify the exposed chemical groups on the substrate surface. Typically, but not exclusively, plasma and UV are used to increase hydrophilicity of hydrophobic substrates (they induce the formation of hydrophilic hydroxyl – OH groups on the substrate surface).

Ag NPs ink (solvents: alcohols and polyalcohols) printed on PI.
Solvents: hydrophilic, substrate: hydrophobic



without UV treatment

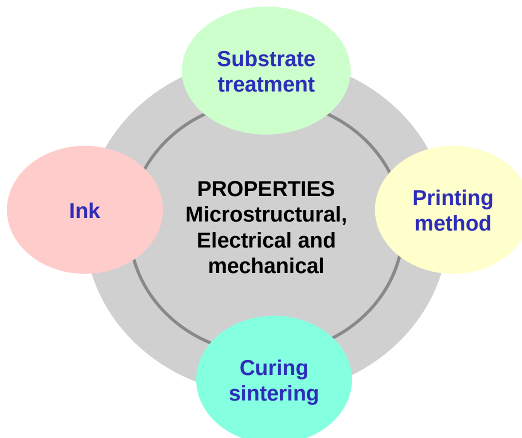
***All-printed OTFT backplanes for flexible electronic paper*, Suzuki et al., ISEP 2010.**



with UV treatment

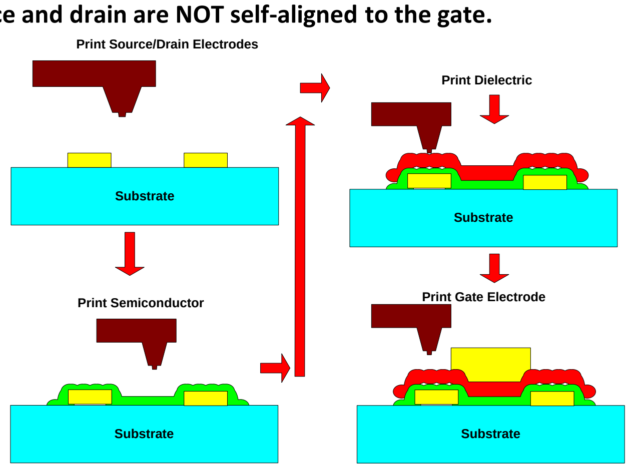
Summary printing

To be successful: Need to find the right combination of parameters



Process Integration: Top-gate TFTs

- **The main driver for TFT use is printing. Conventional “Si-like” top-gate TFT structures are easily made using printing, thought the source and drain are NOT self-aligned to the gate.**



Bottom-gated TFT process flow

- **Analogous to a-Si TFTs, bottom-gated devices can also be realized.**