ISTITUTO ITALIANO DI TECNOLOGIA
CENTER FOR NANO SCIENCE AND TECHNOLOGY

Introduction to Printed Organic Electronics

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PRINTED AND MOLECULAR ELECTRONICS GROUP

"ORGANIC ELECTRONICS - Principles, devices and applications"

7th edition

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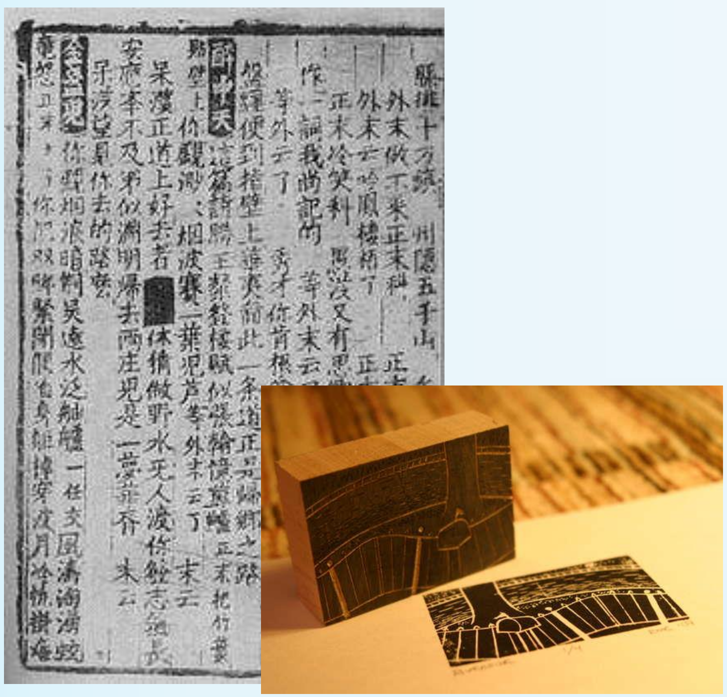
Printing

Printing is a process for reproducing text and images, typically with ink on paper using a printing press.

Source: Wikipedia



Woodblock printing
China, 220 A.D.

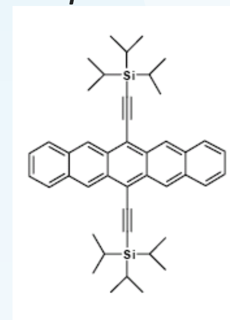
Printing press
Johannes Gutenberg ,1450

Web-fed offset lithographic press at speed
XXth century

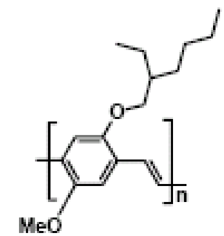
Solution Processable Functional Materials

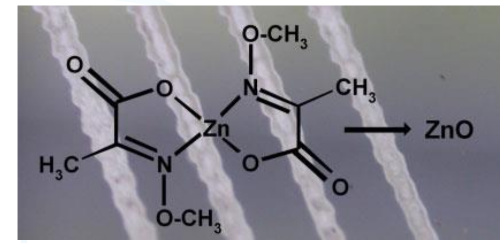
Semiconductors

TIPS-pentacene



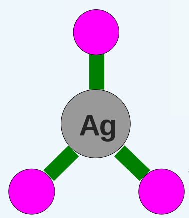
MEH-PPV





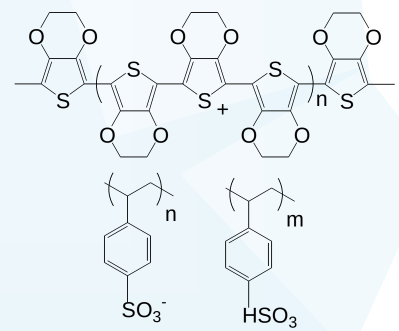
R. C. Hoffmann Phys. Status Solidi A, 1–6 (2010)

Conductors



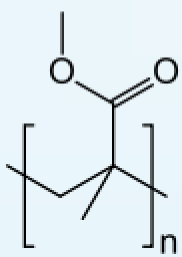
Organic Ligands

Low sintering temperature metallic inks

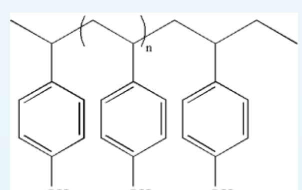


Polymeric conductors

Dielectrics



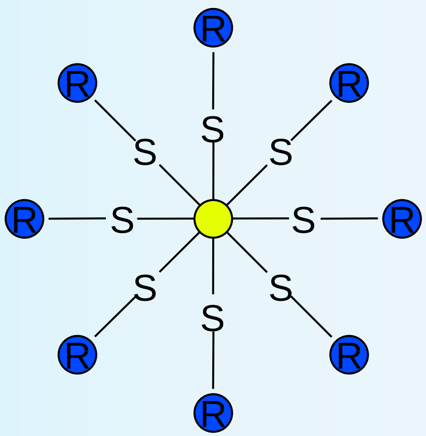
PMMA



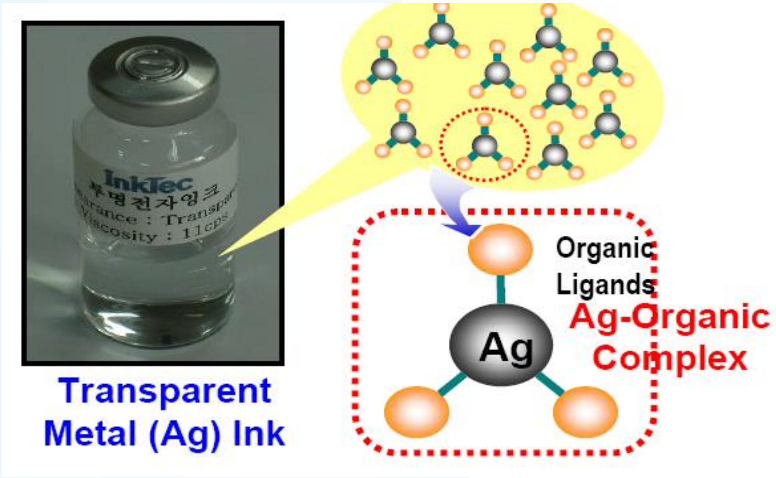
PVP

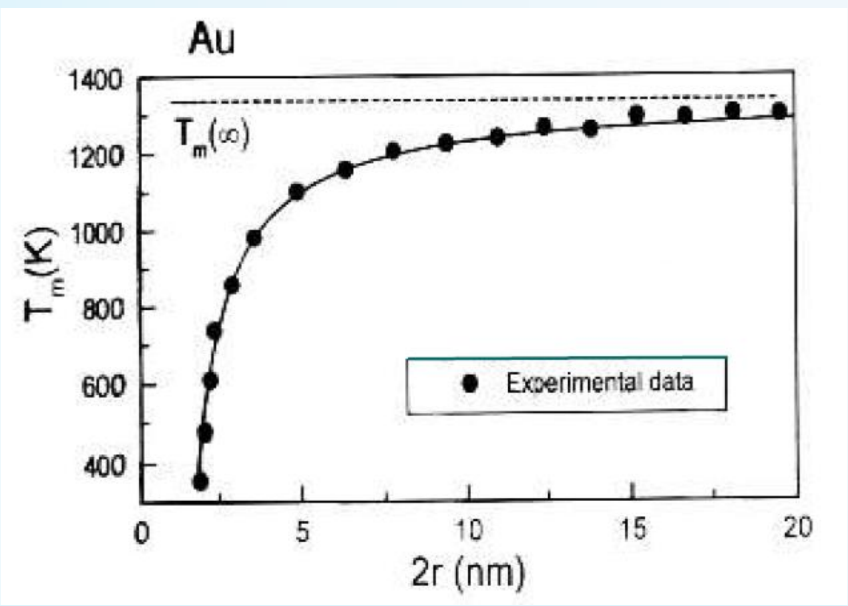
- Possible to formulate "functional inks", with specific electronics properties
- Low temperature processing allow use of plastic substrates

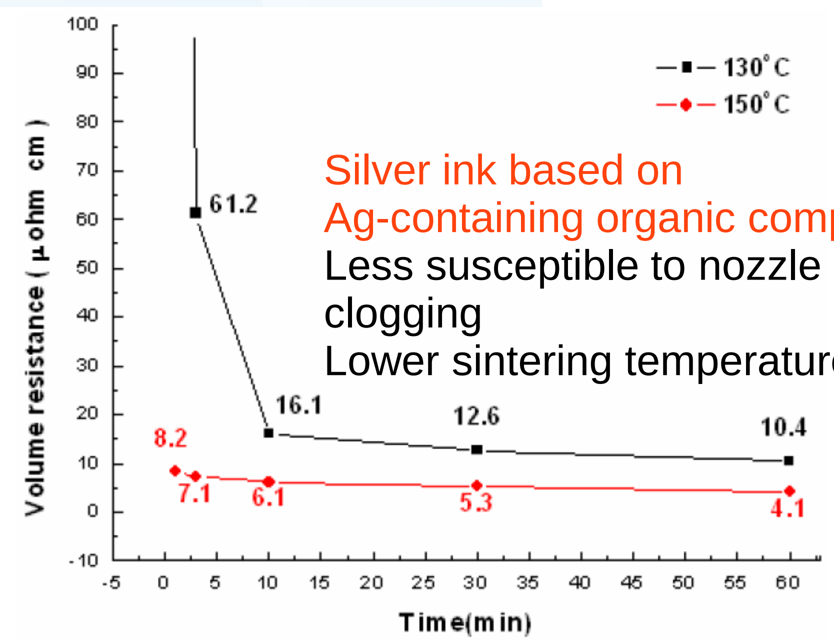
Highly conductive metallic inks



Colloidal gold nanoparticles :
$R = C_4H_9$
Particle size < 5 nm

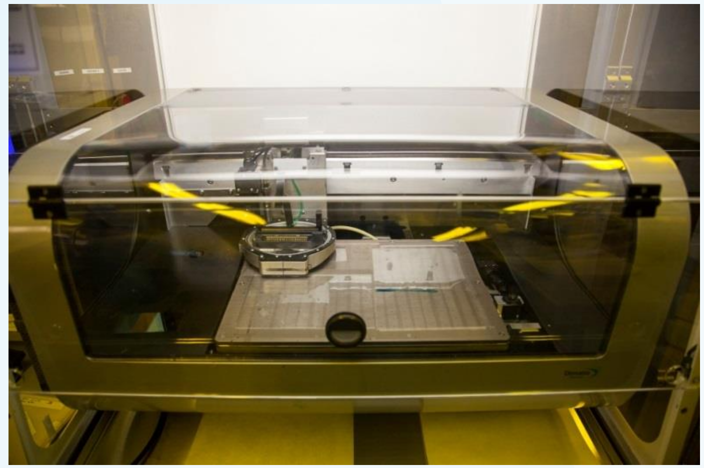


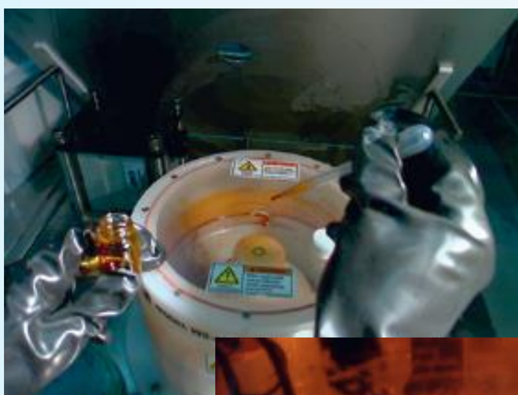




Silver ink based on
Ag-containing organic complex:
Less susceptible to nozzle clogging
Lower sintering temperature

Ph. Buffat and J-P. Borel, Phys. Rev. A, 13, 1976, 2287



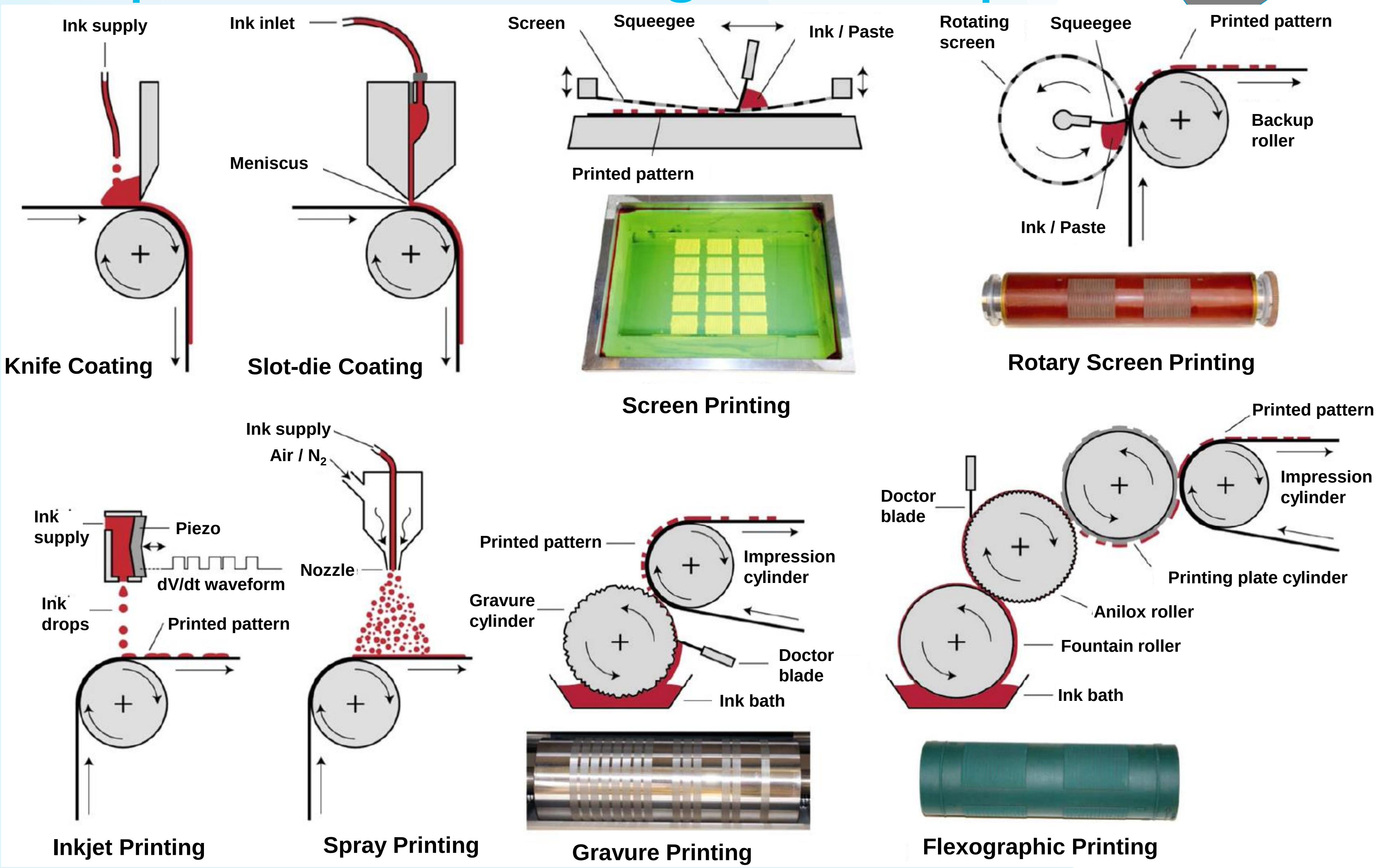


Printed Electronics

OE-A roadmap 2009

New mass markets for low cost, thin and flexible electronics

Graphic Arts Printing Techniques



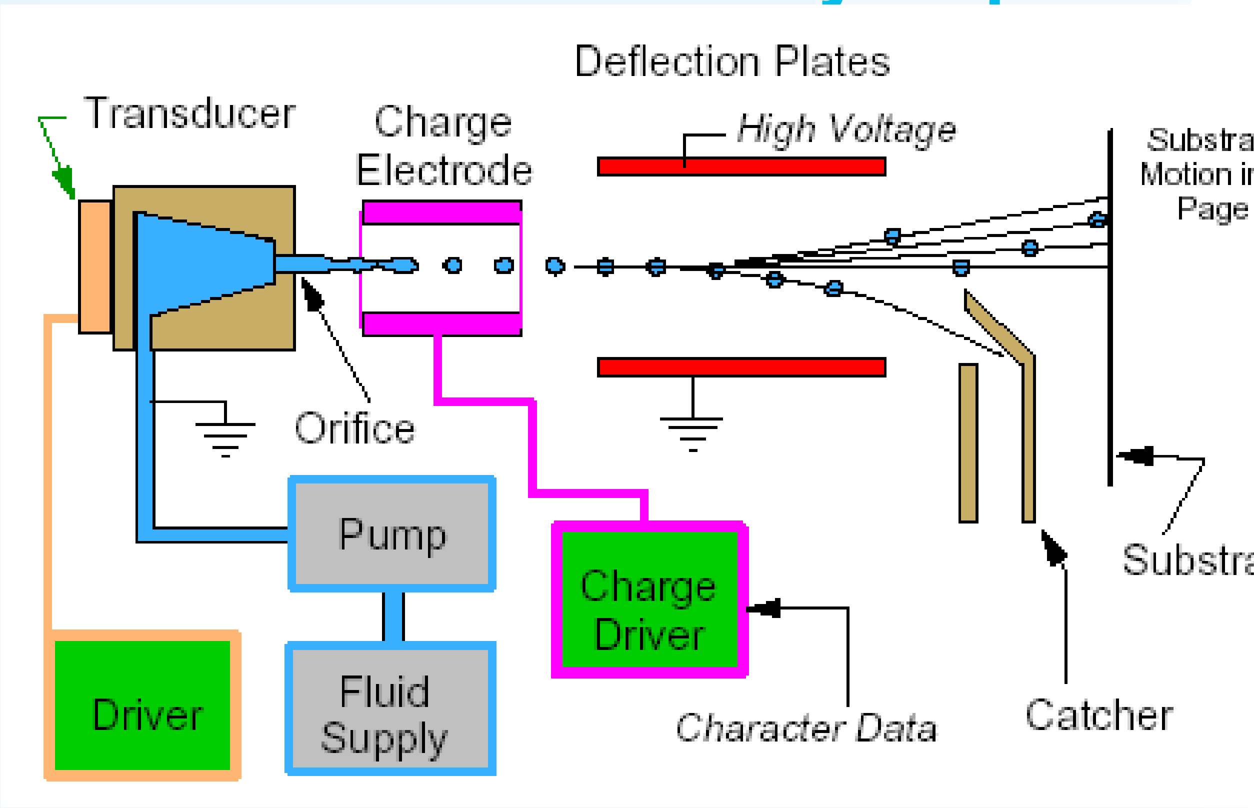
Krebs et al., JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS 2013, 51, 16–34

Graphic Arts Printing Techniques

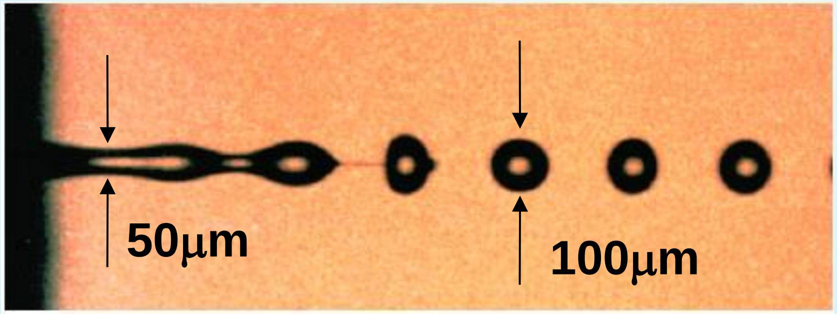
Printing Techniques	Viscosity [Pas]	Thickness [μm]	Feature Size [μm]	Throughput [m^2/s]	Registration [μm]	Features
Flexography	**0.05-0.5**	**0.04-2.5**	**80**	**3-30**	**<200**	Inexpensive plate pattern, high throughput, thick layer / low viscosity ink
Gravure	**0.01-0.2**	**< 0.1–8**	**75**	**3-60**	**>20**	Fast printing, high resolution, relatively high plate cost, low dot gain
Offset	**5-100**	**0.5–2**	**10–50**	**3–30**	**>10**	High quality, high throughput, need for ink additives
Screen	**0.5-50**	**0.015-100**	**20–100**	**2–3**	**>25**	Robust, simple, thick layer, large feature size, high ink viscosity, slow speed
Inkjet	**0.001-0.04**	**0.01-20**	**20–50**	**0.01–0.5**	**5–20**	Non-contact, small ink quantities, digital printing, low viscosity ink, slow speed

Inkjet Printing

Continuous mode inkjet printing



Water jet, 20kHz

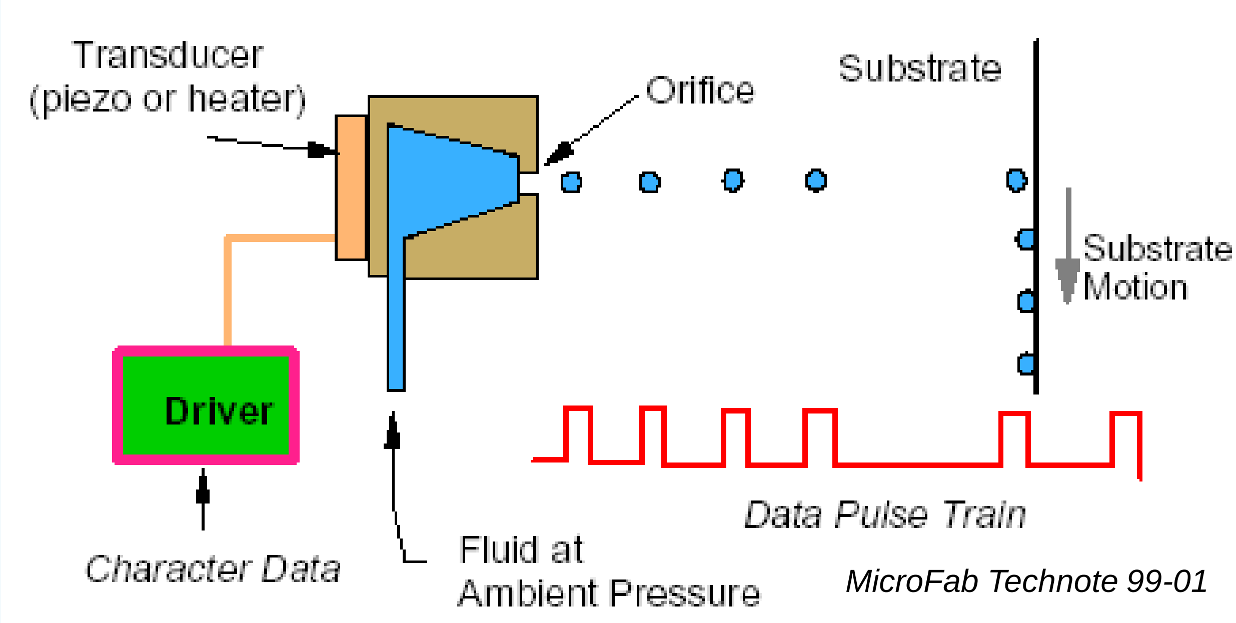


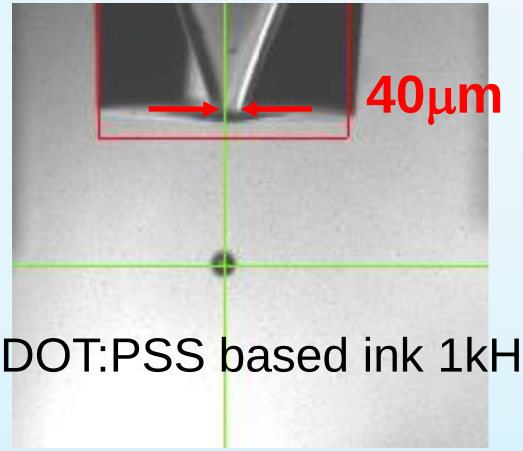
- High ink velocity: ≈ 50 m / s
- Typical droplet diameter: 150µm
- Typical rate: 80-100kHz, up to 1MHz
- Industrial market applications, product labeling – high throughput

MicroFab Technote 99-01

Drop-On-Demand (DOD) mode

Drops produced by electromechanically induced pressure waves – *Hansell 1950*



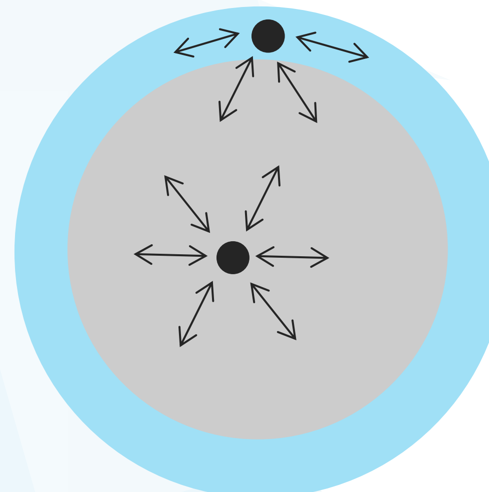


PEDOT:PSS based ink 1kHz

- Simple system, no recirculation
- More energy to produce a droplet
- Typical rate: tens of kHz
- Smaller drop size, higher placement accuracy
- Low-end printer market

Surface Tension

For solids and more general: “Surface Energy”



•It is a force for unit length
(1N/m = 1000 dyne/cm)
or equivalently energy per area (J/m^2)

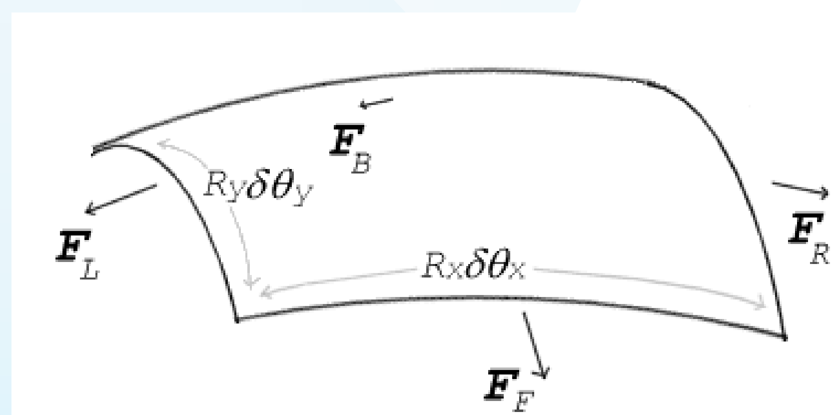
•It is caused by cohesive forces

•It develops at the interface between two different immiscible fluids or at the interface between a fluid and a gas

Young-Laplace Equation

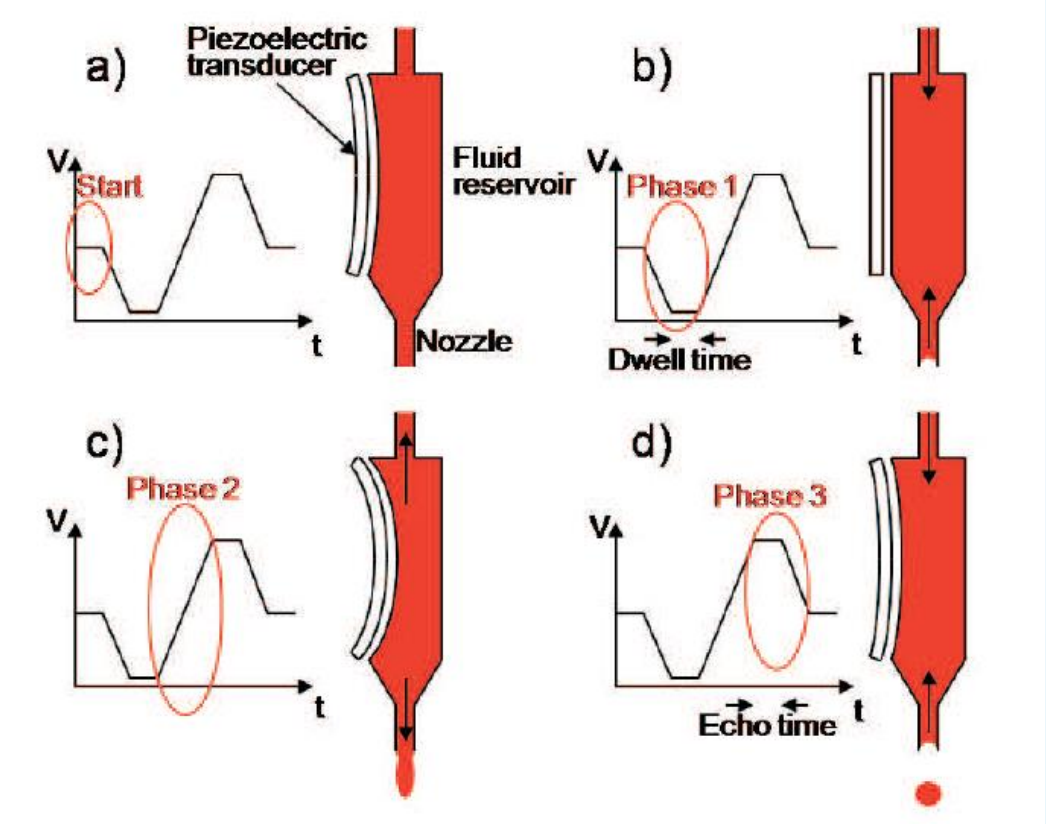
$$\Delta p = \gamma(R_x^{-1} + R_y^{-1})$$

T dependent: $\gamma = \gamma^o \left(1 - \frac{T}{T_C}\right)^n$



Δp: pressure difference; γ: surface tension; R_x and R_y: principal curvature radii

Piezoelectric DOD technology

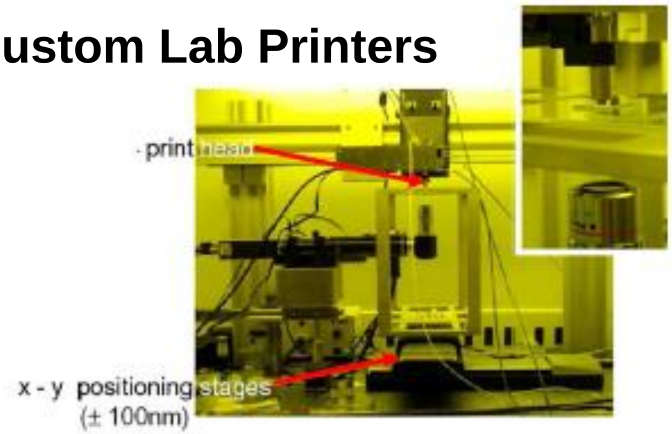


- Suited to a variety of solvents
- Epson Stylus 800 (1993)
- Minimum internal diameter of the nozzle: **≈ 10 µm (1pl)**
- Susceptible to **clogging**

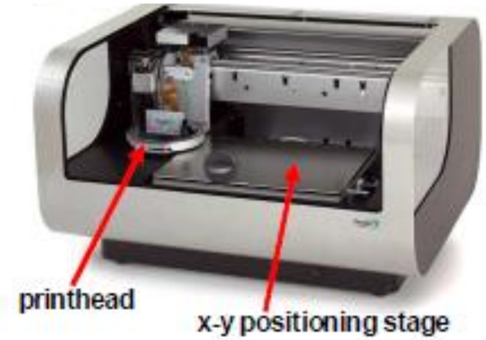
The deflection of a piezoelectric transducer generates an acoustic wave in the printhead cavity, which causes the break off of a drop from the nozzle

Research and Commercial Printers

Custom Lab Printers

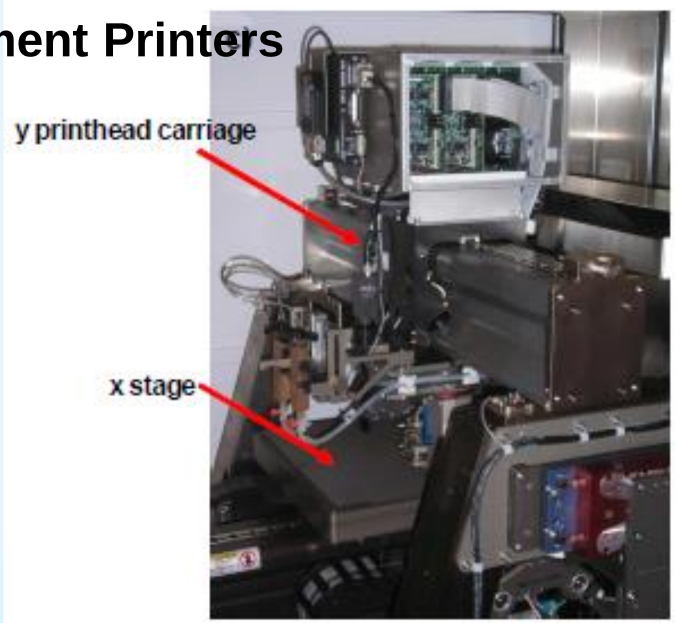


Prototyping and Ink Testing Printers



Dimatix Materials Printer

Development Printers

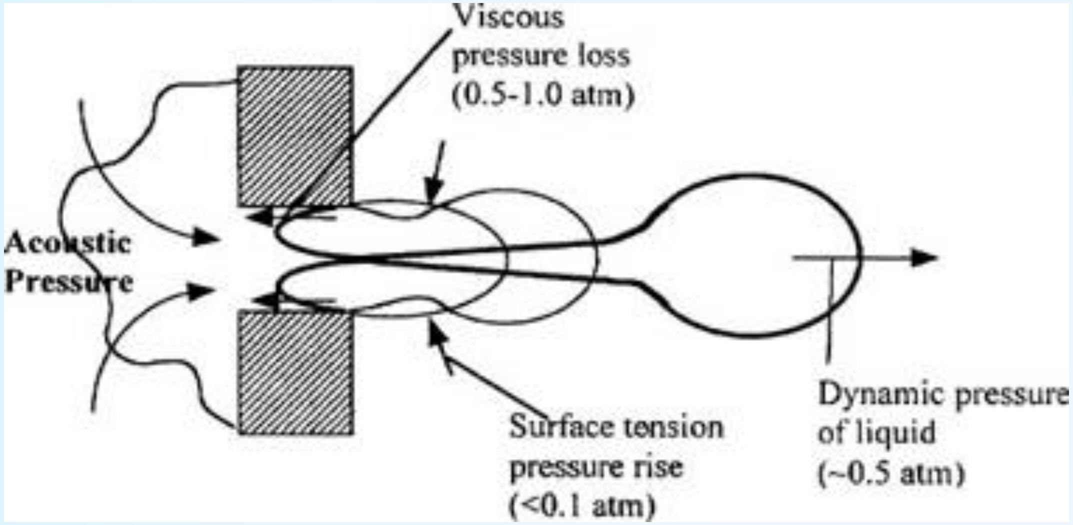


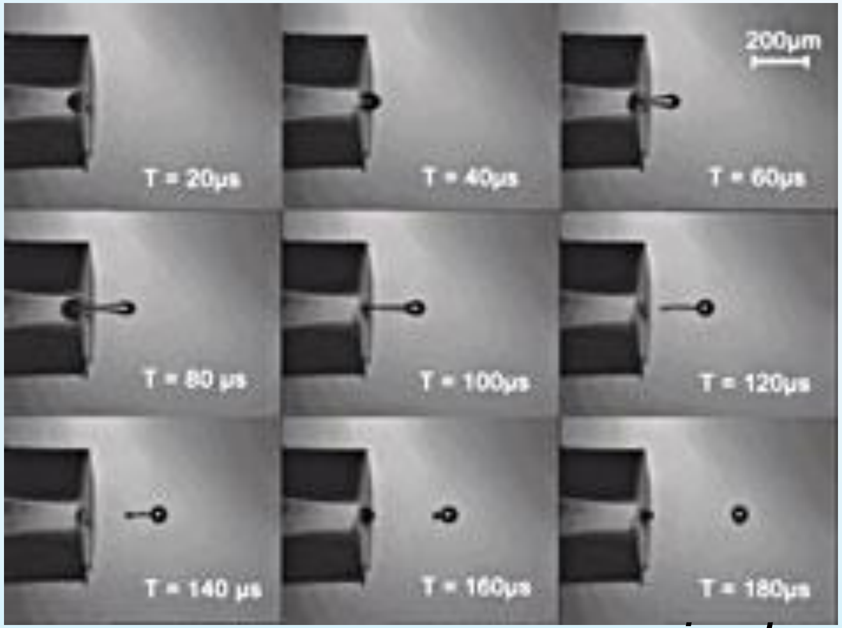
LITREX 120L

Production Printers

LITREX M-Series Generation 8 (2400 mm X 2400 mm)

Jet stabilization





microdrop

Key points

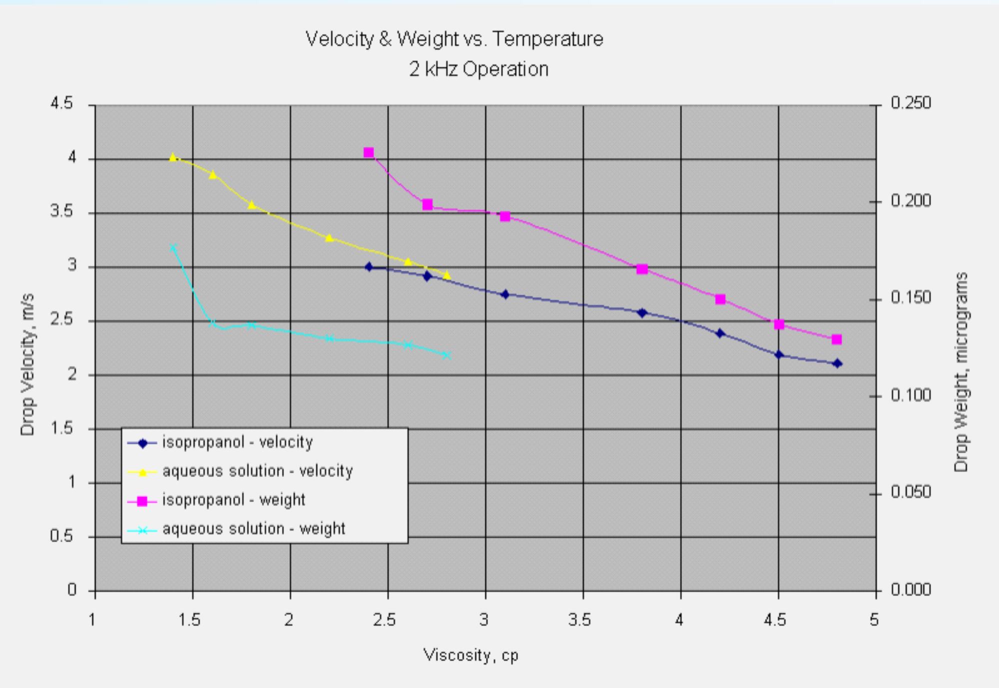
- Ink compatibility (*solvent, particles size < 1/100 nozzle diameter*)
- Ink viscosity
- Ink boiling temperature
- Ink surface tension

Ink Viscosity

Accepatable range: 0.5-20 mPa•s

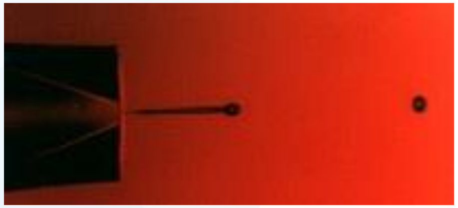
(1 mPa•s = 1 cP)

Higher the viscosity,
higher acoustic waves dampening



water: 0.89 mPa•s
xylene: 0.93 mPa•s
ethanol: 1.07 mPa•s
mercury: 1.53 mPa•s
olive oil: 81.x mPa•s

Higher the viscosity,
less satellites formation



Ethylene glycol, 18 mPa•s

Isopropanol, 2 mPa•s

MicroFab Technote 99-02

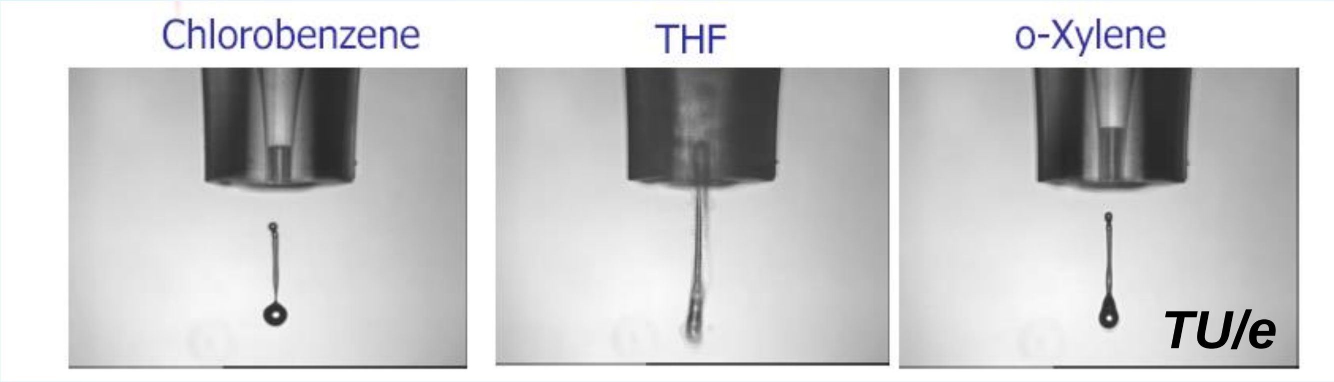
Ink surface tension and boiling point

Surface Tension

Acceptable Range: 20-70 mN•m^{-1}

ethanol: 22.3 mN•m^{-1}
xylene: 28-30 mN•m^{-1}
olive oil: 32 mN•m^{-1}
water: 72.8 mN•m^{-1}
mercury: 465 mN•m^{-1}

Solvent volatility, "sufficiently" low



Bp: **132°C** **66°C** **144°C**

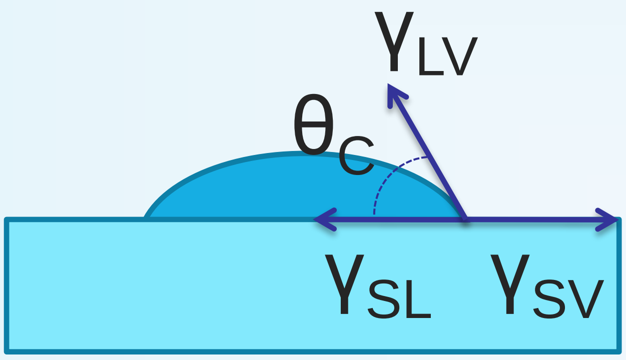
U.S. Schubert, TU/e

MEH-PPV, 2.5 mg/mL

M_n = 40k-70k g/mol

Contact Angle

Interfacial tensions



Young equation

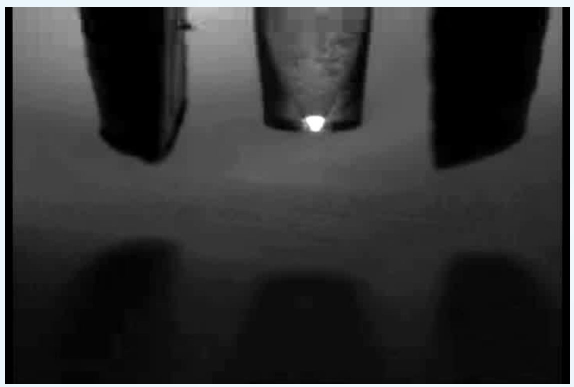
$$\gamma_{SV} - \gamma_{SL} - \gamma_{LV}\cos\theta_C = 0$$

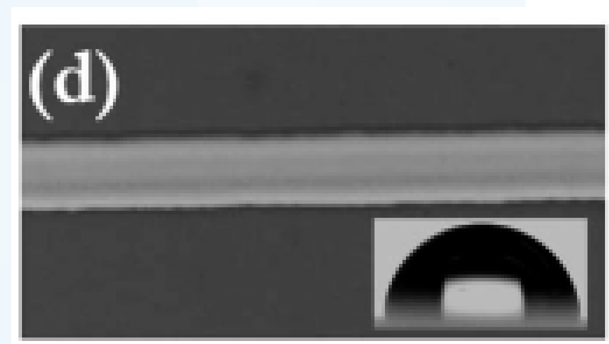
- Results of the interplay between adhesion and cohesion forces
- The higher the surface tension of the liquid, the higher the contact angle
- The higher the surface energy of the solid, the lower the contact angle

Surface energy and line stability

- *Substrate surface energy* vs. *ink surface tension*: "wettability", line width, line stability…

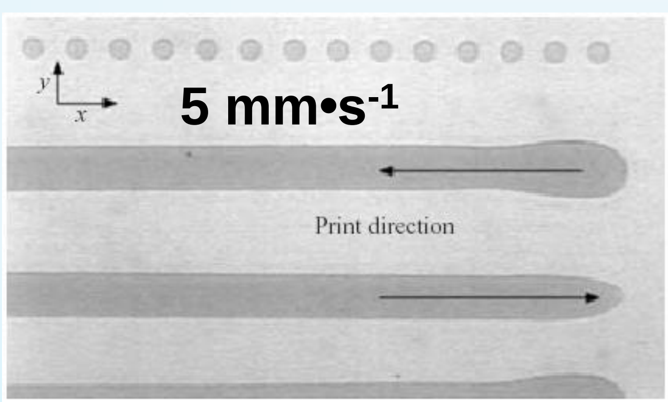
Ag metallic ink on perfluorinated polymer

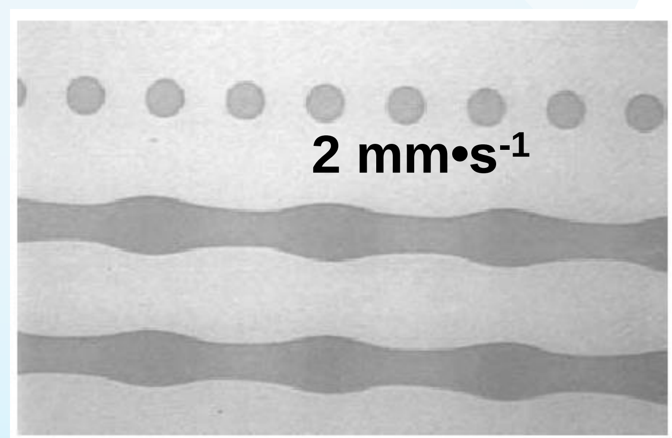




Whiting et al., APL 95 (2009) 253302

- *Droplet ejection rate / substrate velocity*





Duineveld, J. Fluid. Mech. 477 (2003) 175

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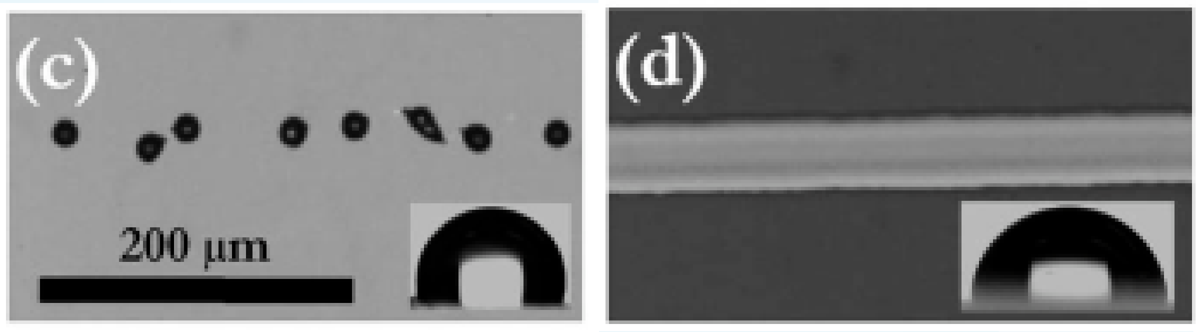

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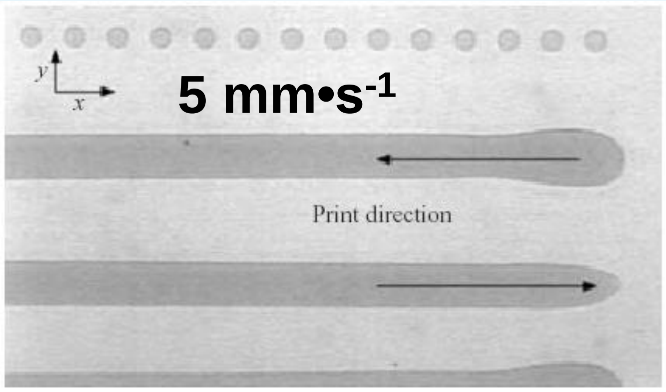
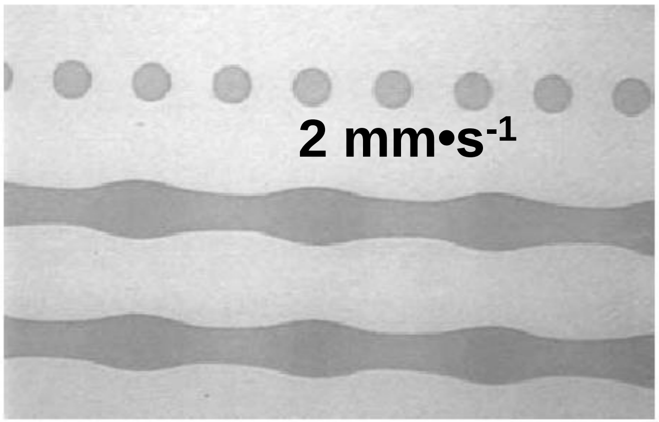


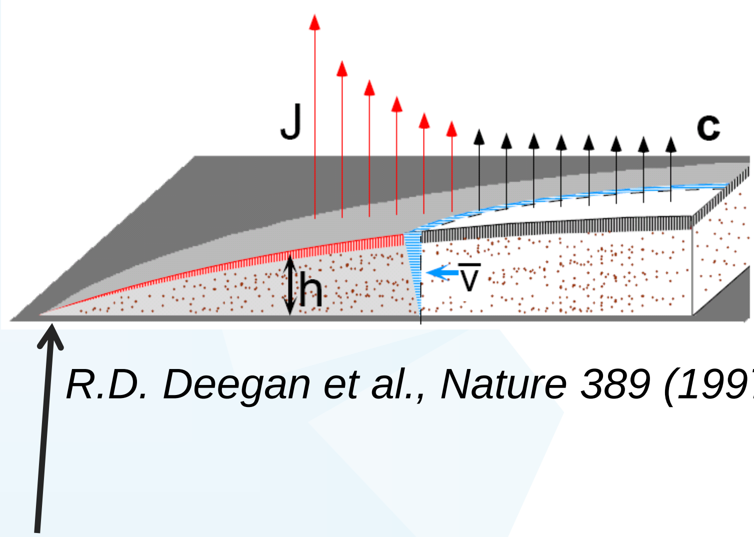


Duineveld, J. Fluid. Mech. 477 (2003) 175

Coffee stain effect

- "Coffee stain" effects lead to inhomogeneous thickness

floreo.com



R.D. Deegan et al., Nature 389 (1997)

Pinning of the line due to surface imperfections / impurities or self-pinning

Evaporating flux

$$J = -D \nabla \phi$$

$$J \propto (R - r)^{-\lambda}$$

$$\lambda = (\pi - 2\theta_C) / (2\pi - 2\theta_C)$$

$\phi(r)$: vapour concentration profile
D: vapur diffusitivity in air
R: radius
r: distance from the edge

Marangoni Flow

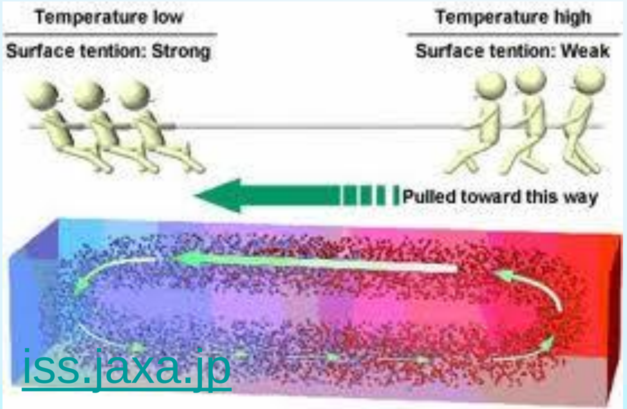
•Caused by a gradient in surface tensions

•Molecules of a liquid with higher surface tensions pull stronger than molecules of a liquid with lower surface tension

Marangoni number $M = \Delta\gamma L / \eta D$

Schubert at al., Langmuir, 20 (2004) 7789

L: length scale
η: viscosity
D: diffusion coefficient

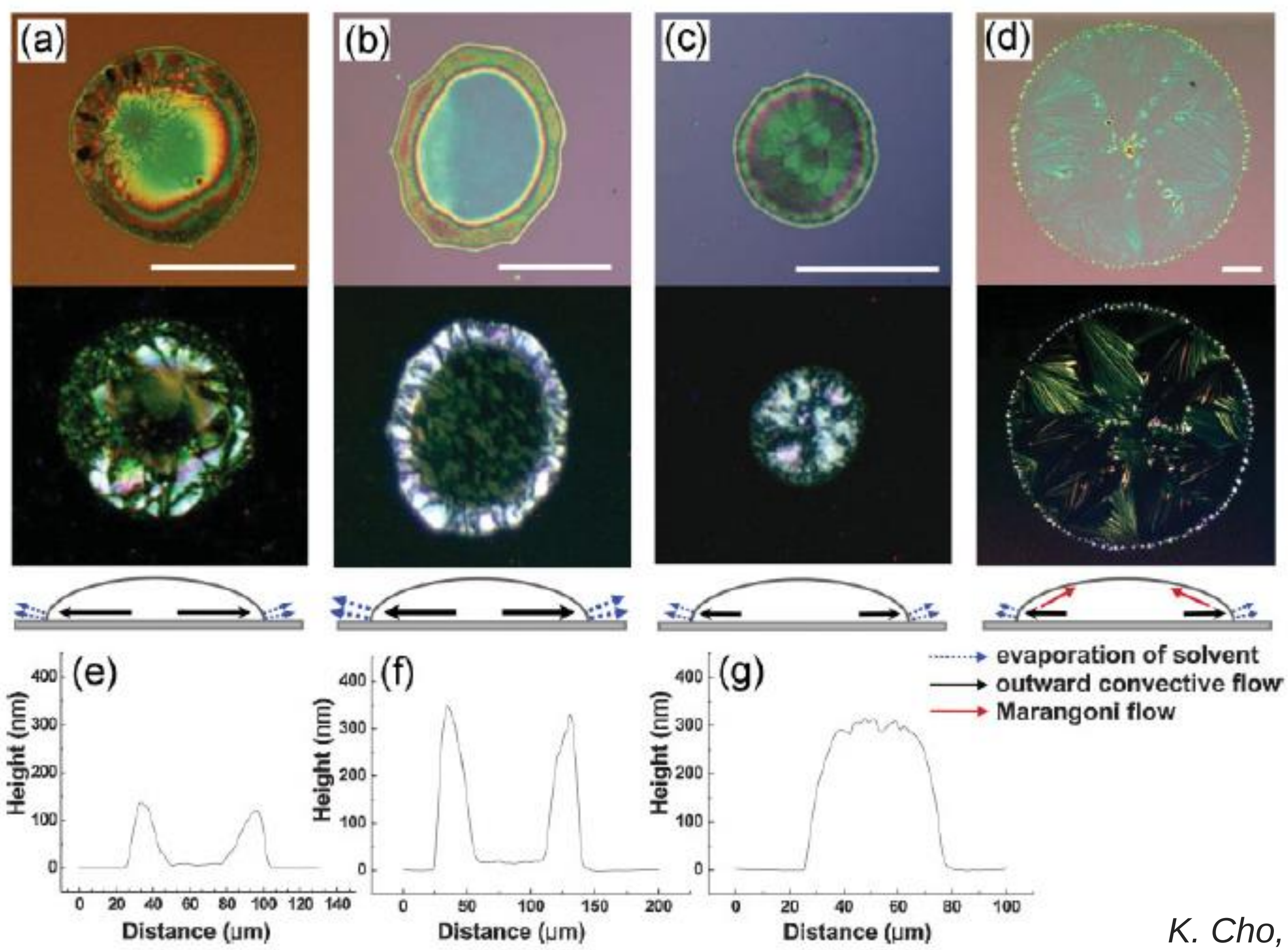


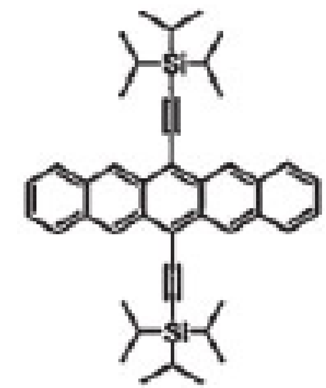
iss.jaxa.jp

E.g.: “wine tears”

Controlling Flows

Solvent properties	Major solvent	Minor solvent added at 25 vol%		
	Chlorobenzene	Hexane	o-Dichlorobenzene	Dodecane
	CB	Hex	DCB	Dod
Boiling point [°C]	131.1	68.8	180	216
Surface tension (γ) [dyn cm^{-1}]	33.6	18.4	36.6	25.3



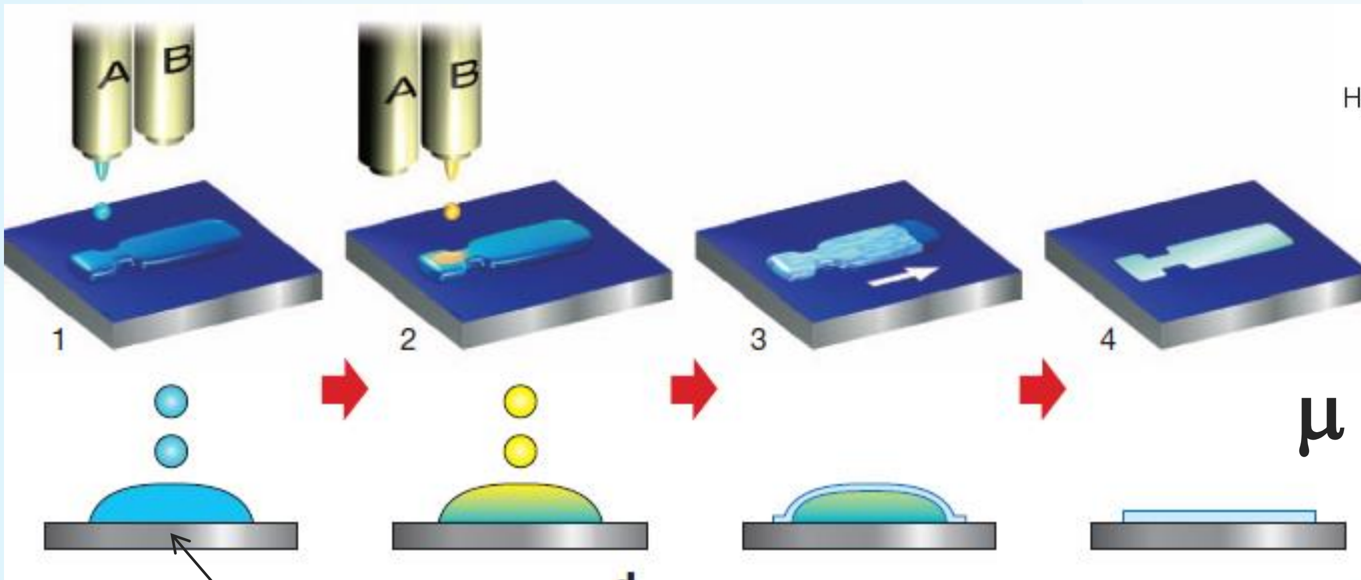


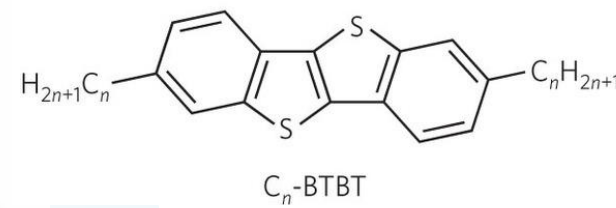
TIPS-pentacene

a+e : 100% CB
b+f : 75% CB + 25% Hex
c+g : 75% CB + 25% DCB
d : 75% CB + 25% Dod

K. Cho, Adv. Funct. Mater. 19 (2009) 1515

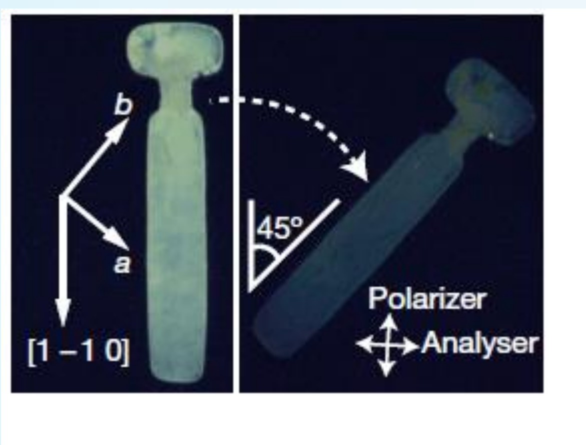
Inkjet Printed Single Crystals

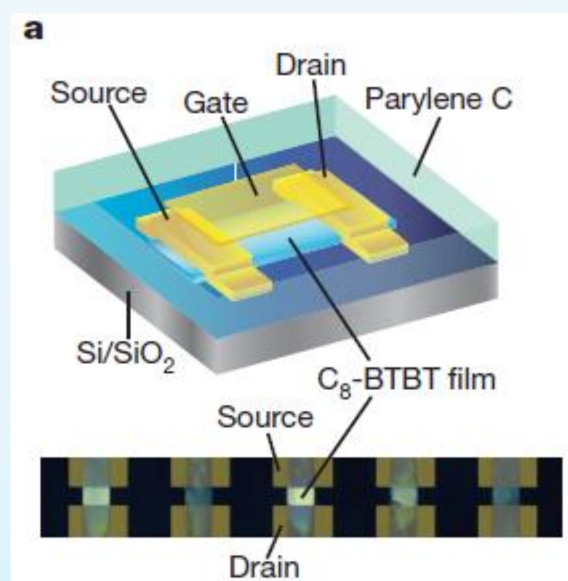


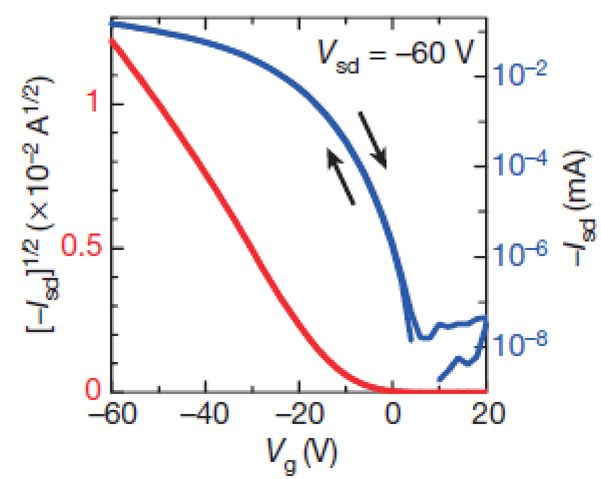


μ = 16 cm²/Vs

antisolvent

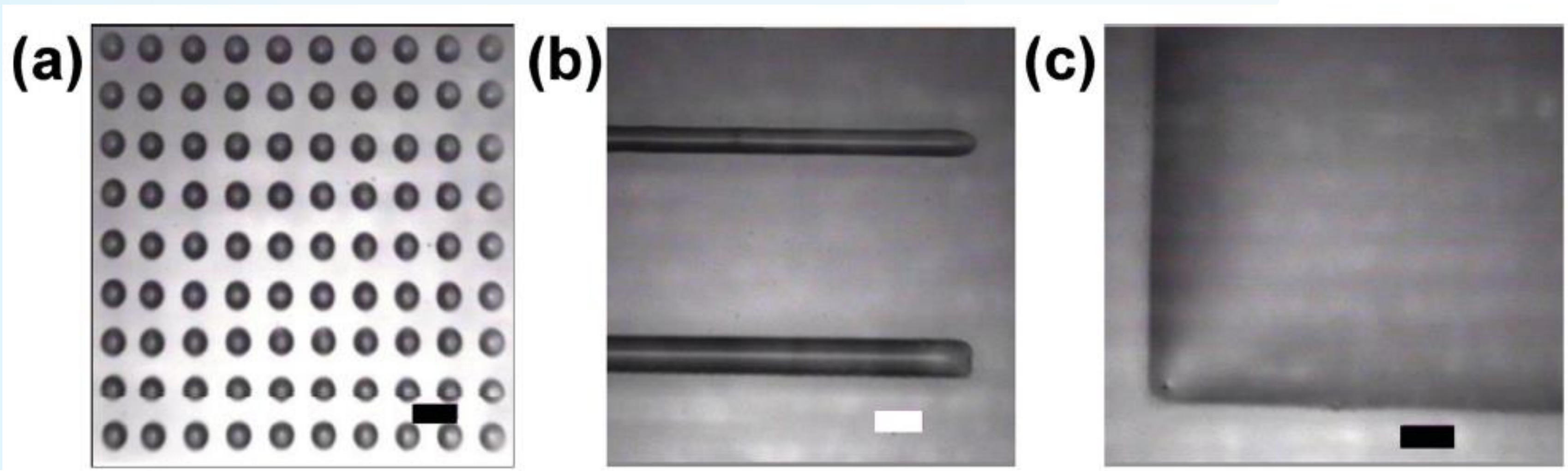


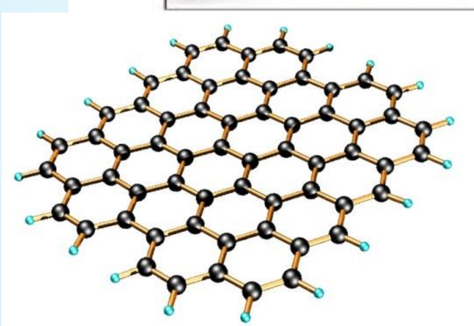


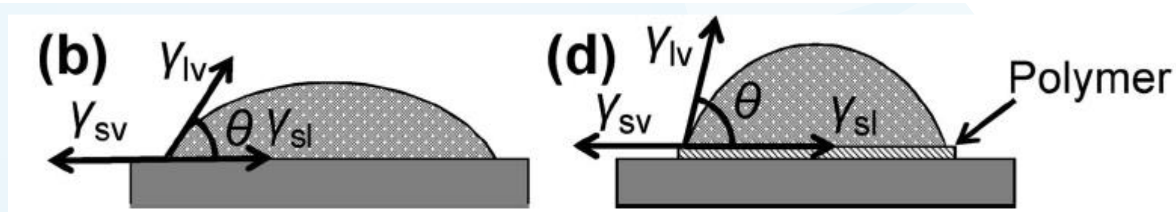


Minemawari et al., Nature 475 (2011) 364

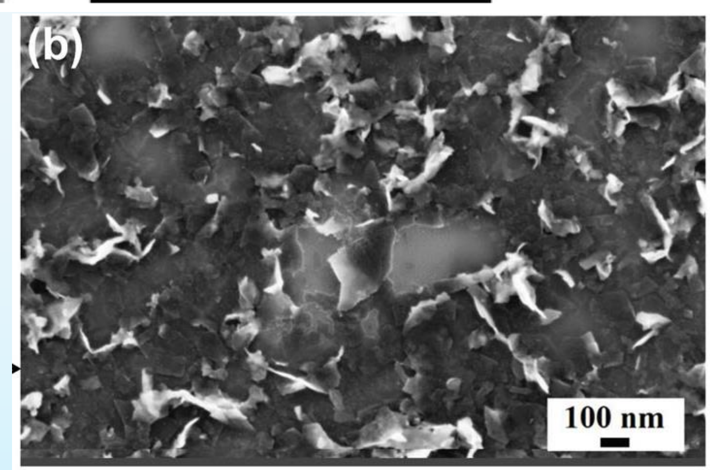
Inkjet Printing of “Graphene”







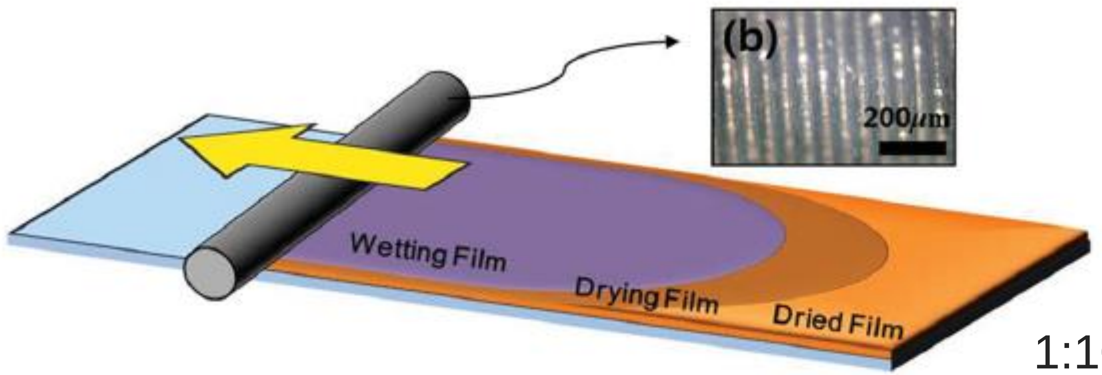
- Exfoliation of graphite flakes in DMF
- Addition of ethyl cellulose
- Solvent exchange: terpineol
- Polymer can be removed at 300 – 400 °C, 1 h
- Resistivity down to 30 kΩ/□

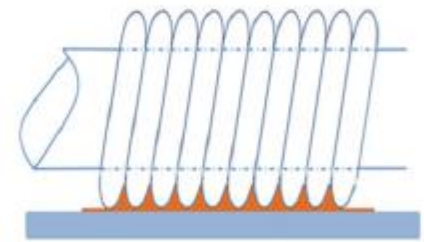


Jiantong Li , et l. Adv. Mater. ***2013,*** DOI: 10.1002/adma.201300361

Other Printing Techniques and Applications

Bar-coating





1:10 ratio between the wet film thickness and wire diameter

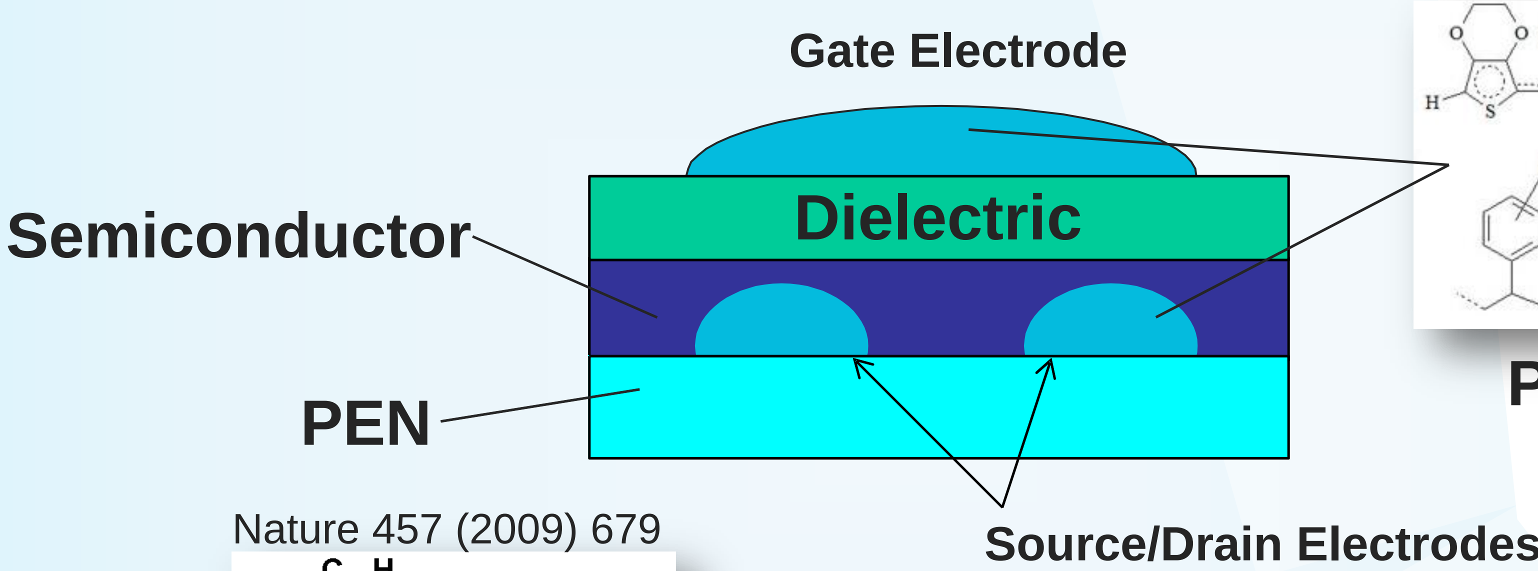
- Very simple technique
- Precise control of thickness down to few tens of nm
- Large range of viscosities
- Deposition of ink stripes

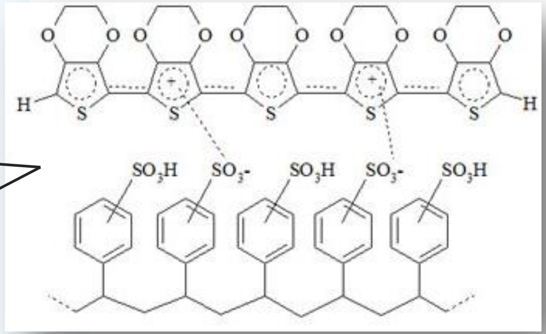
Limitations:
- 0 to 1 dimensional patterning
- strong influence of process and fluid parameters

rdspecialties.com

Y.Y. Noh *et all.*, *Adv. Mater.* ***2013,*** DOI:10.1002/adma.201205330

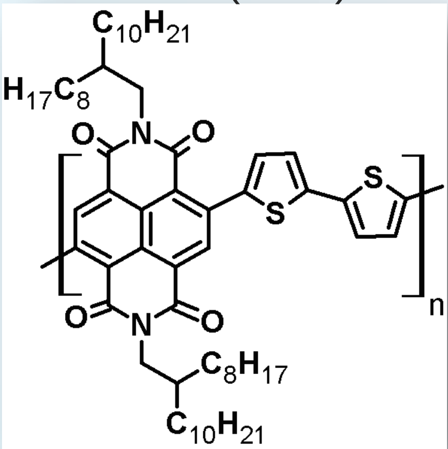
All-Printed, All-Organic FET





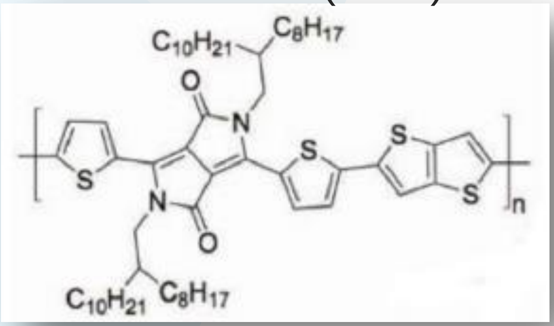
PEDOT:PSS

Nature 457 (2009) 679



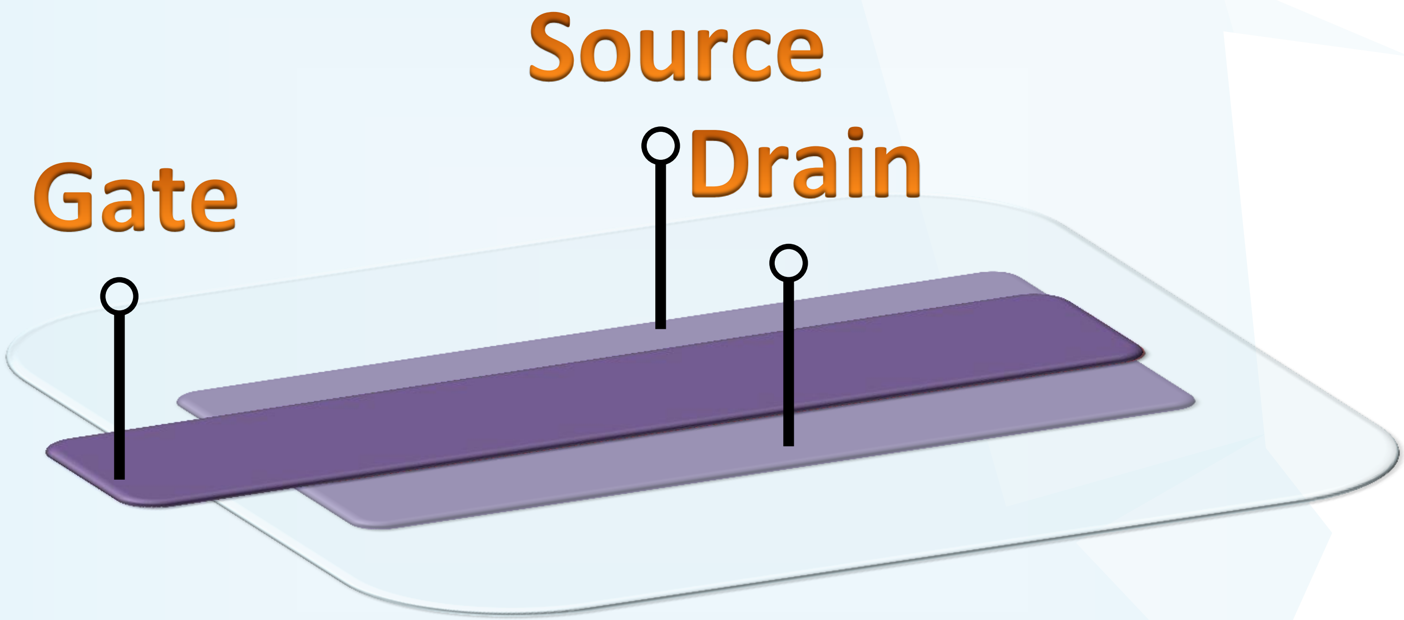
P(NDI2OD-T2) [Polyera N2200]
N-type co-polymer
Mobility (spin coated): 0.1 – 1 cm²/Vs

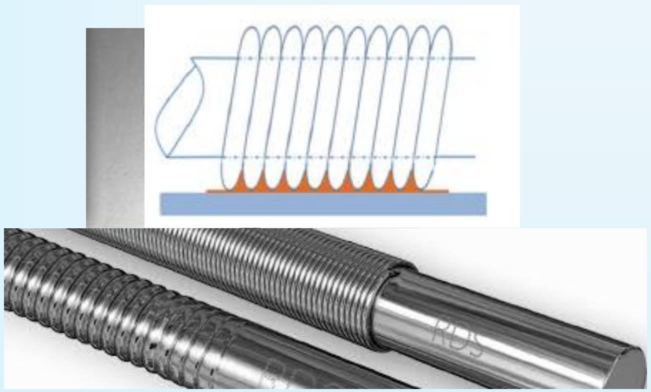
Adv. Mater. 24 (2012) 647

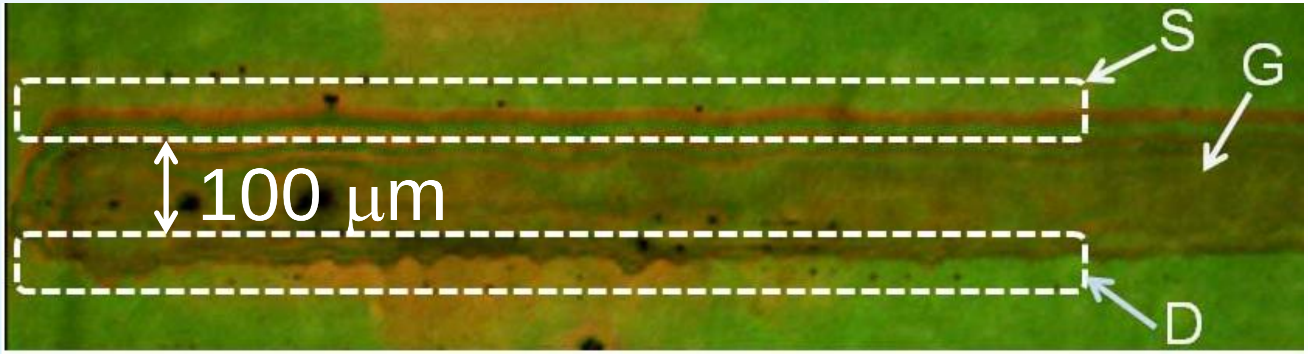


DPPT-TT
P-type (ambipolar) co-polymer
Mobility (spin coated): 0.1 - 1 cm²/Vs

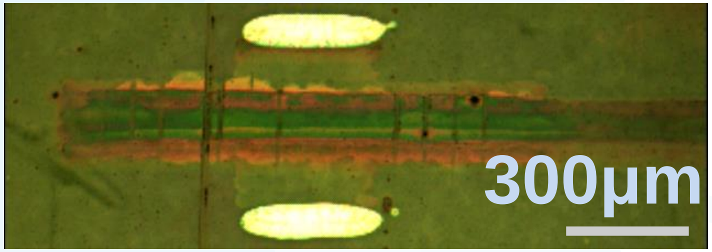
All-Printed, All-Organic FET

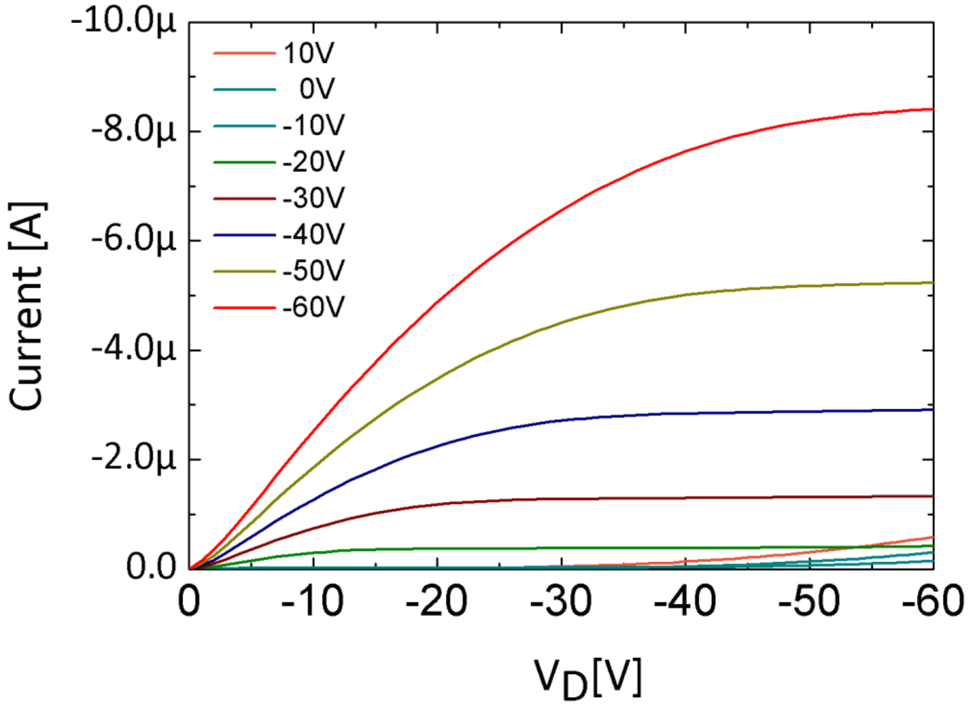


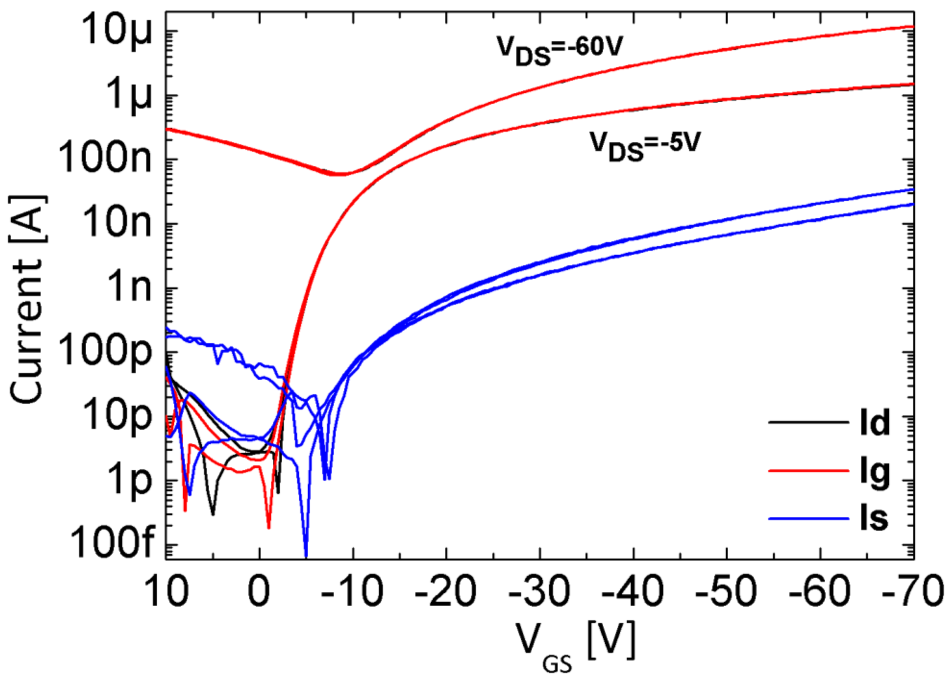




p-type OFETs





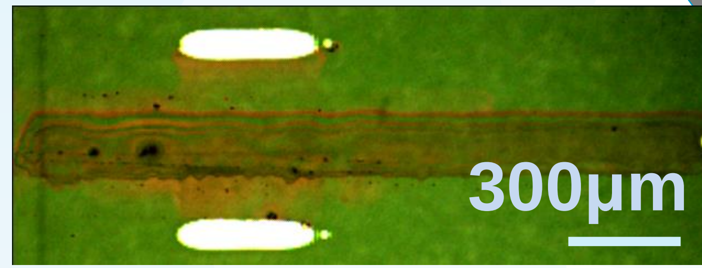


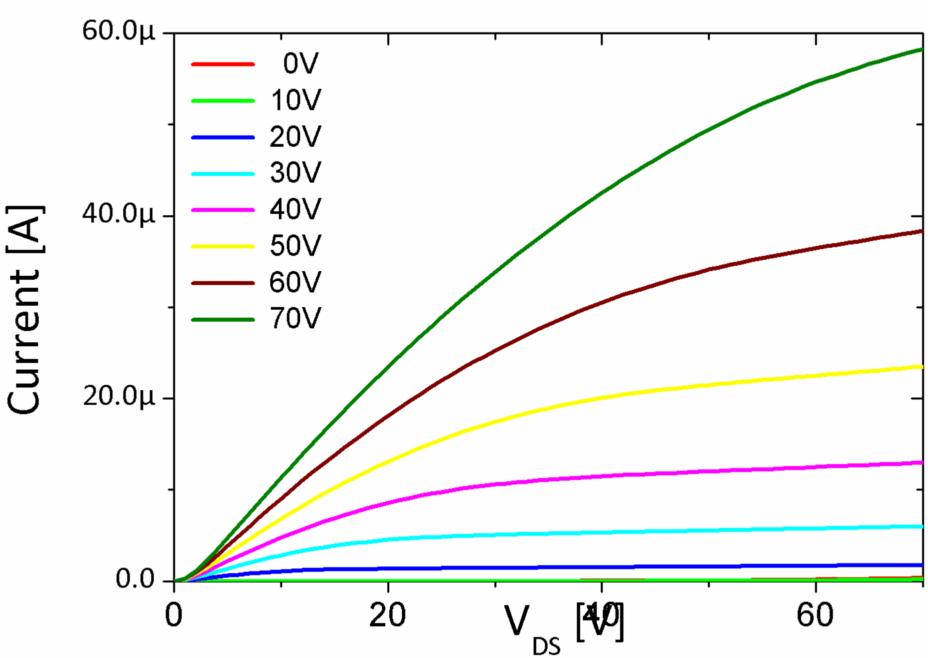
L = 115 µm, W = 1200 µm

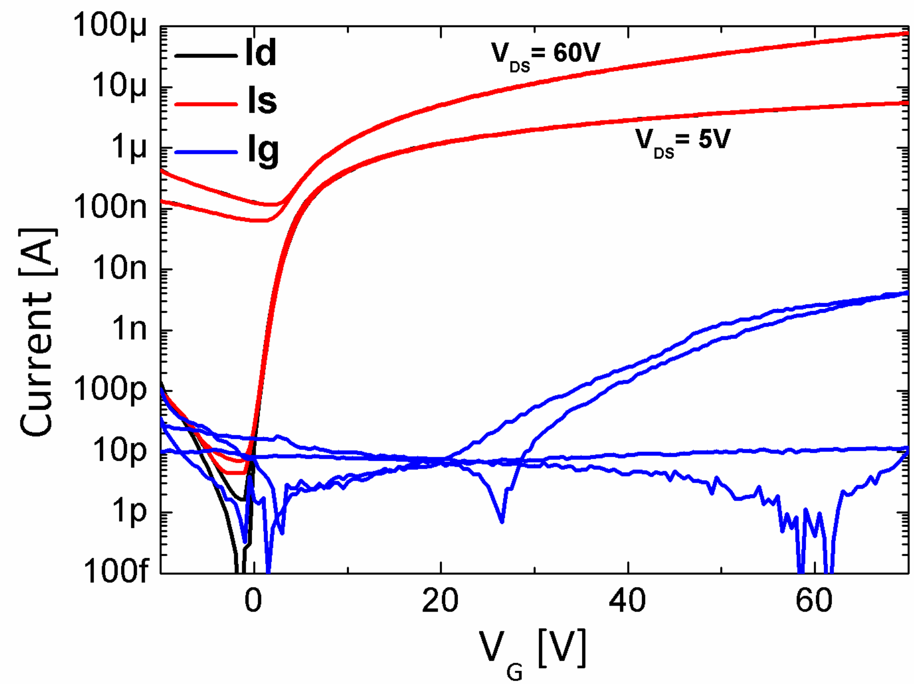
Mobility(sat)= 0.2 cm^2/Vs, Threshold Voltage =-7.3V

n-type OFETs

R_c down to 30 kΩcm



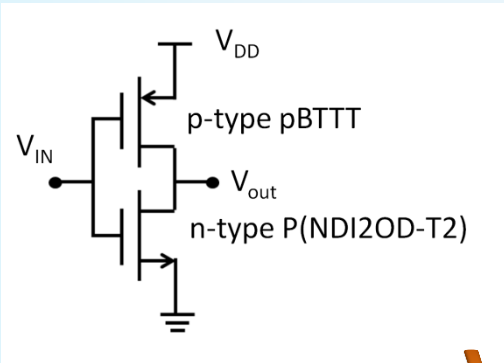


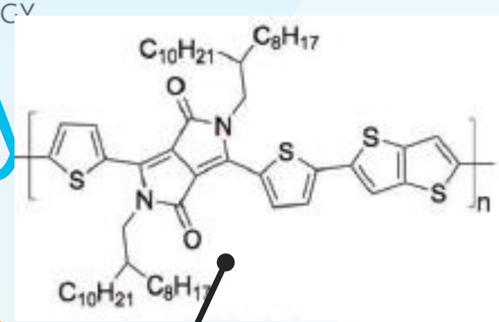


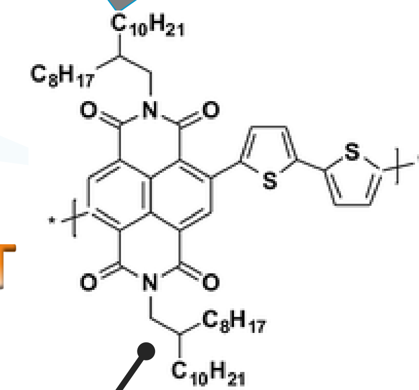
L = 50 µm, W = 1200 µm

Mobility(sat)= 0.2 cm^2/Vs, Threshold Voltage = 4.7V

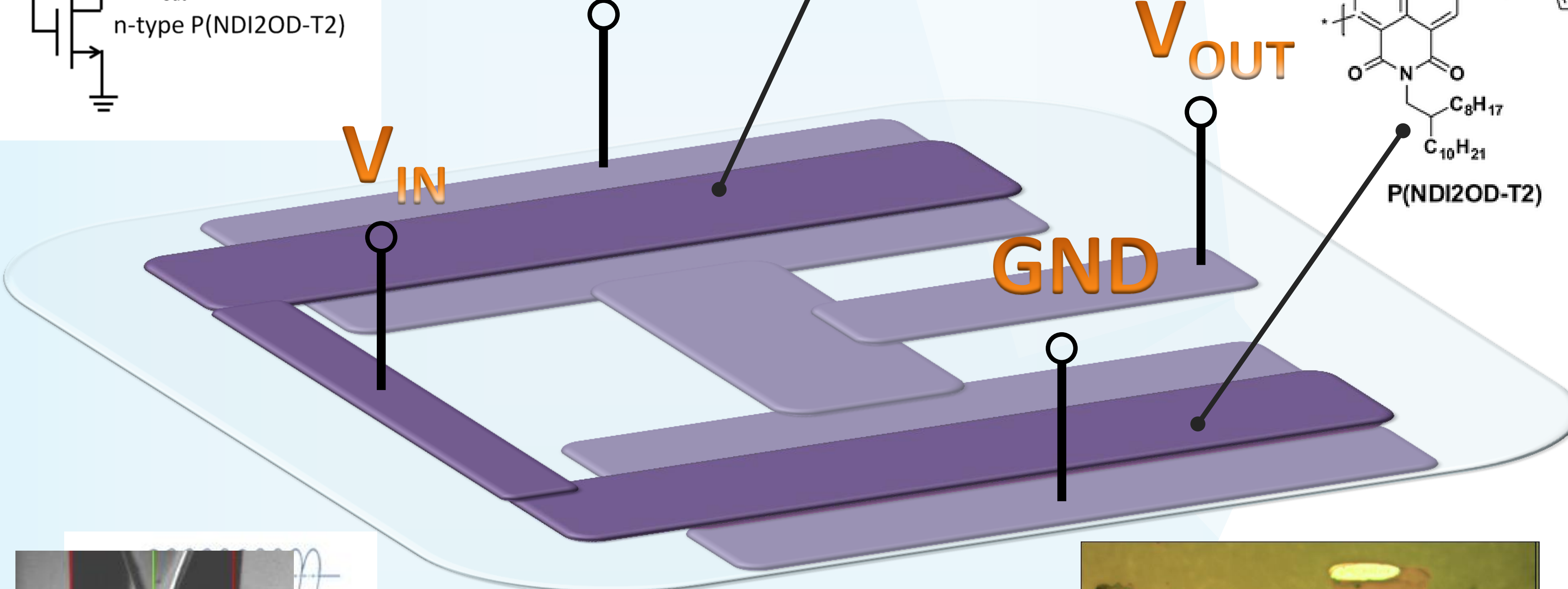
Complementary

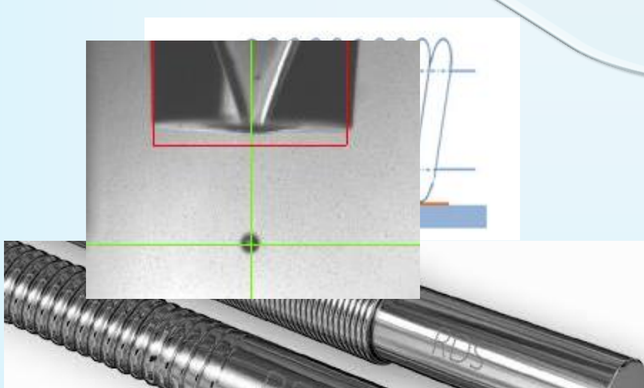


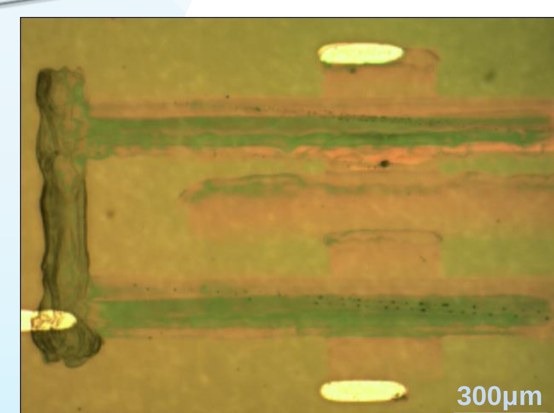




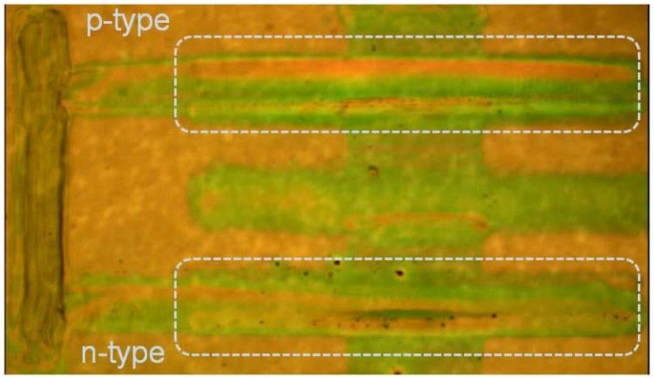
P(NDI2OD-T2)

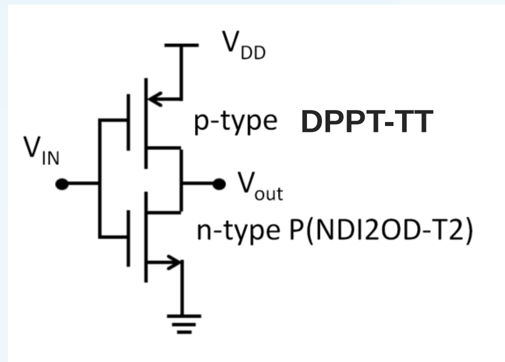


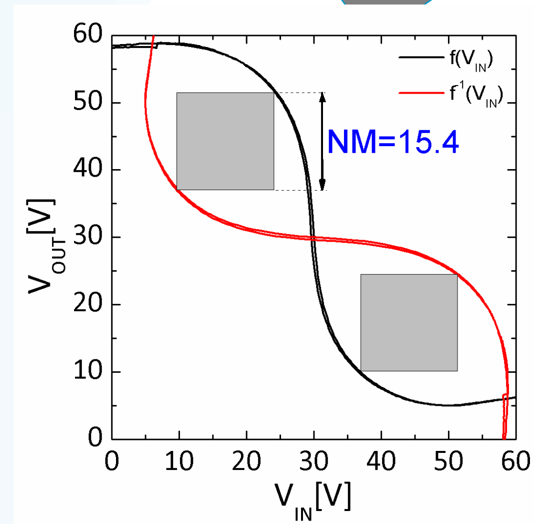


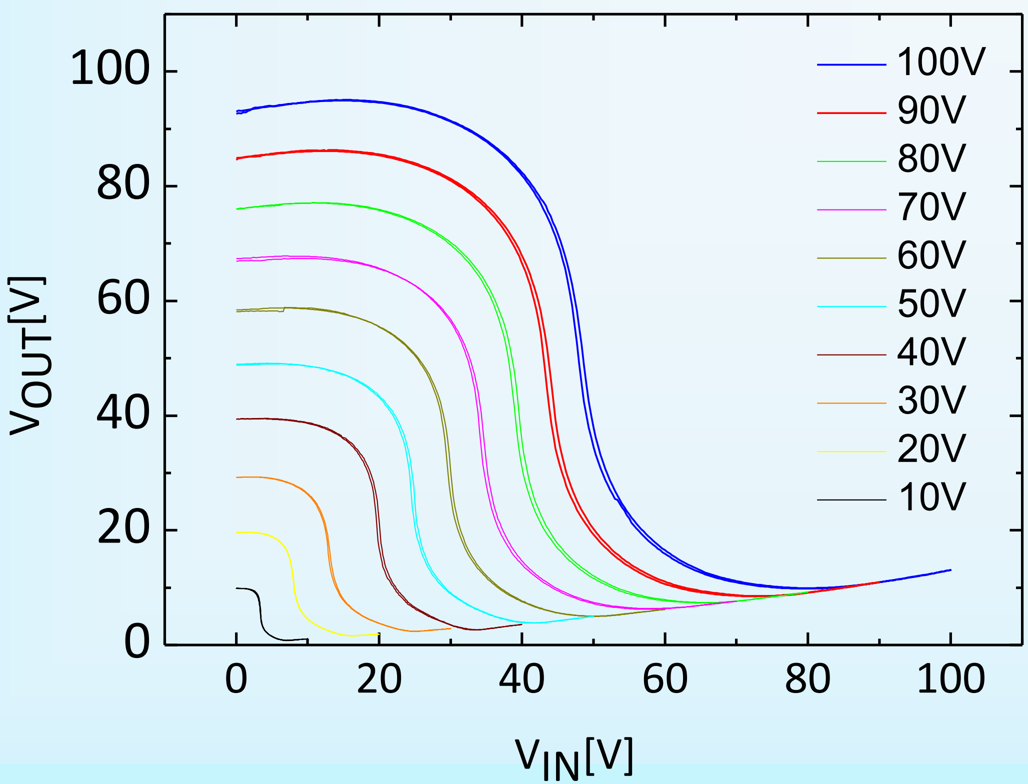


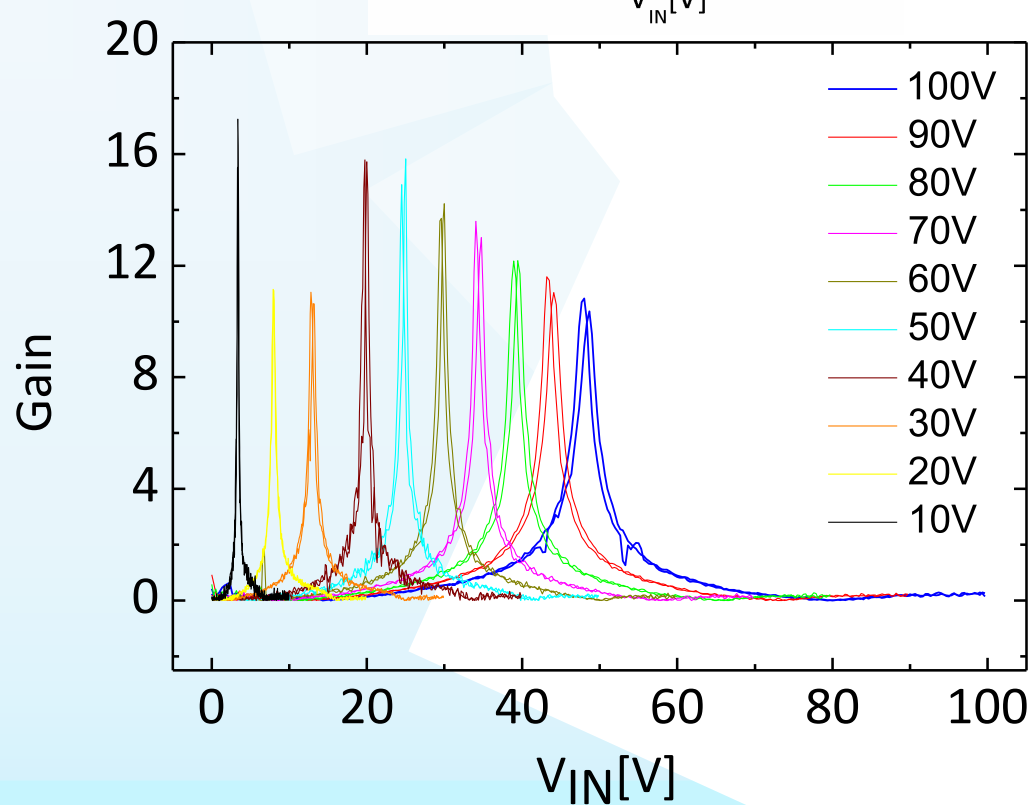
Complementary Inverter



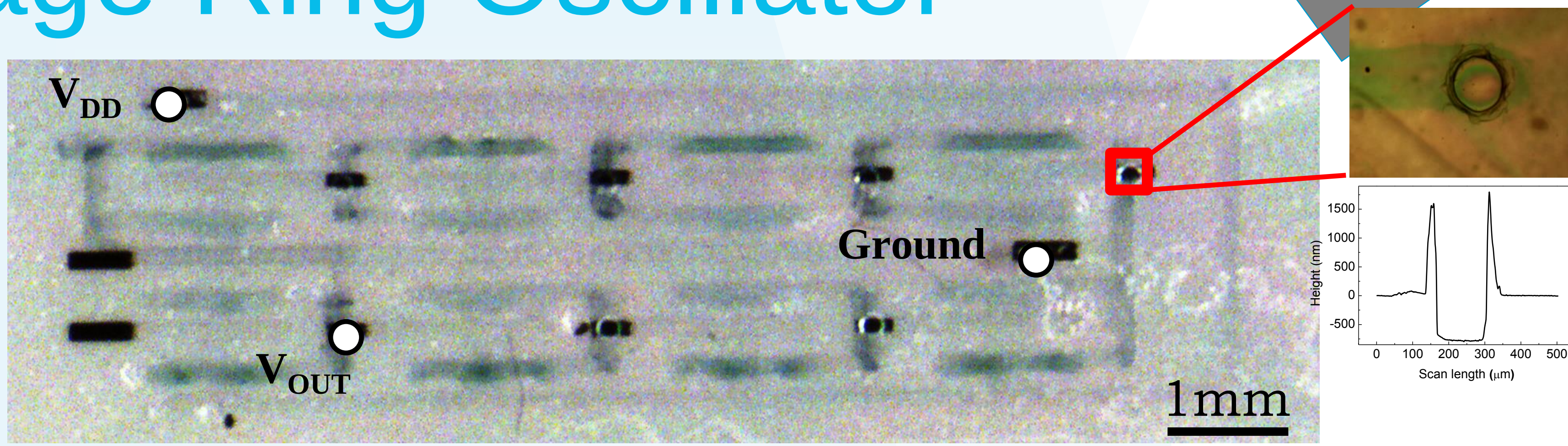




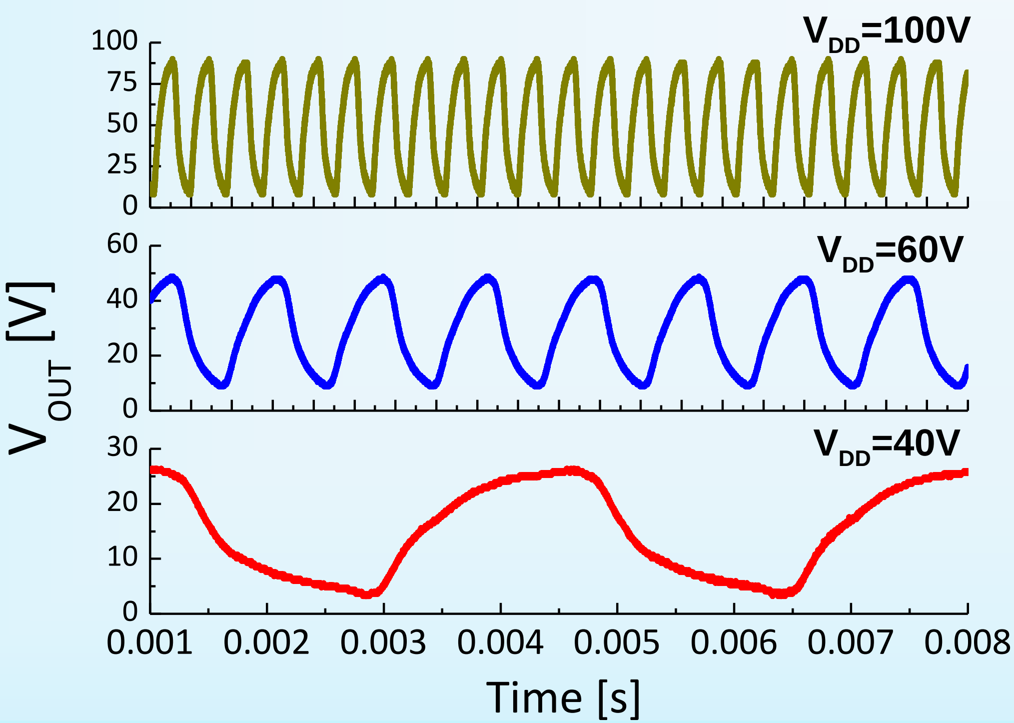


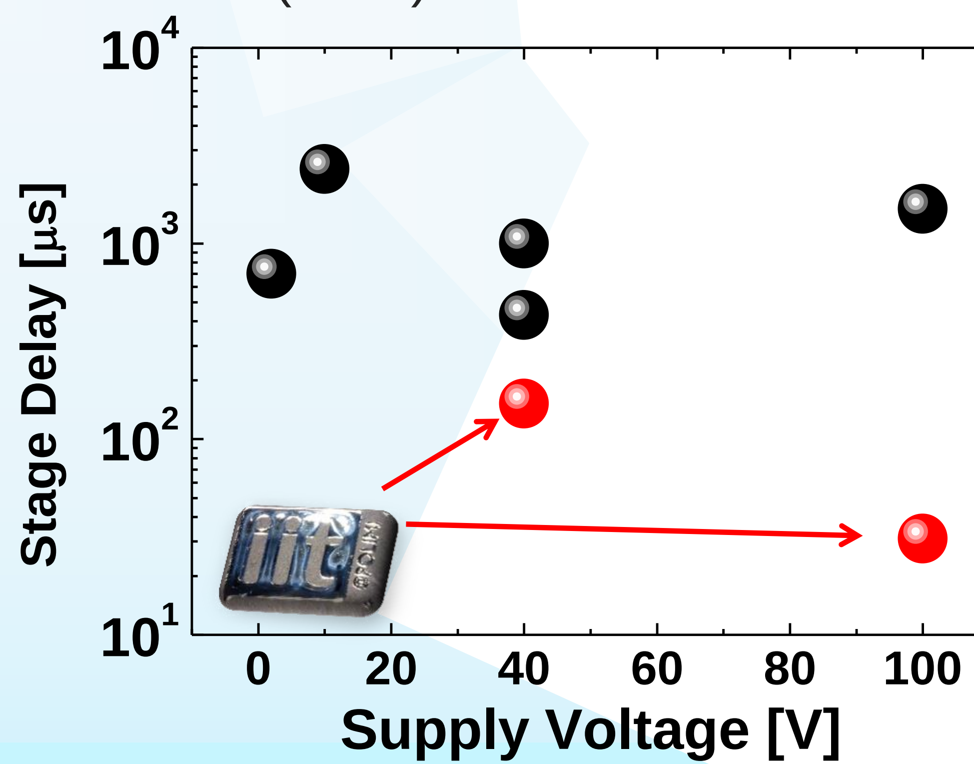


7-stage Ring Oscillator

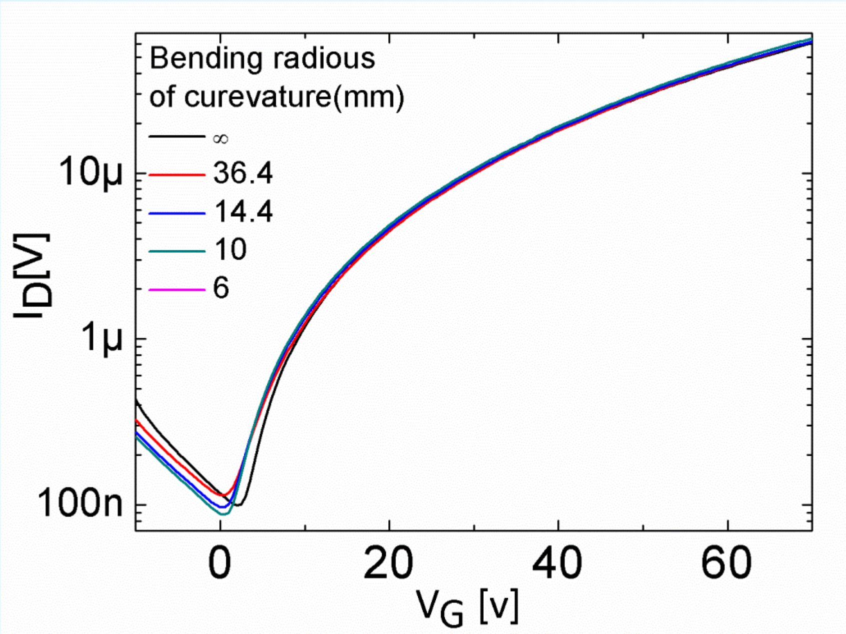


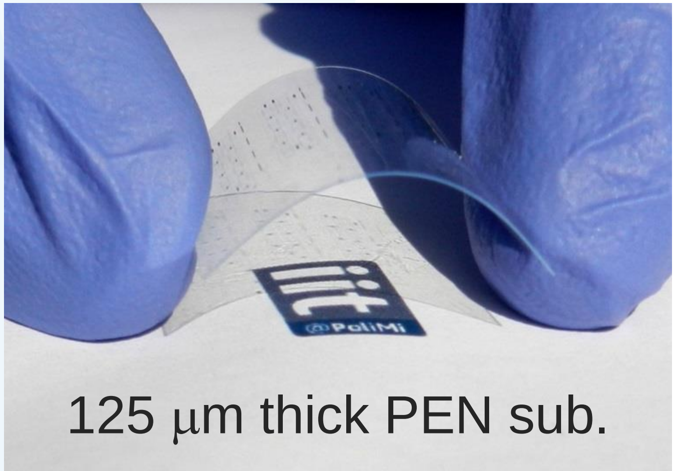
S. Mandal et al., Organic Electronics 20 (2015) 132-141

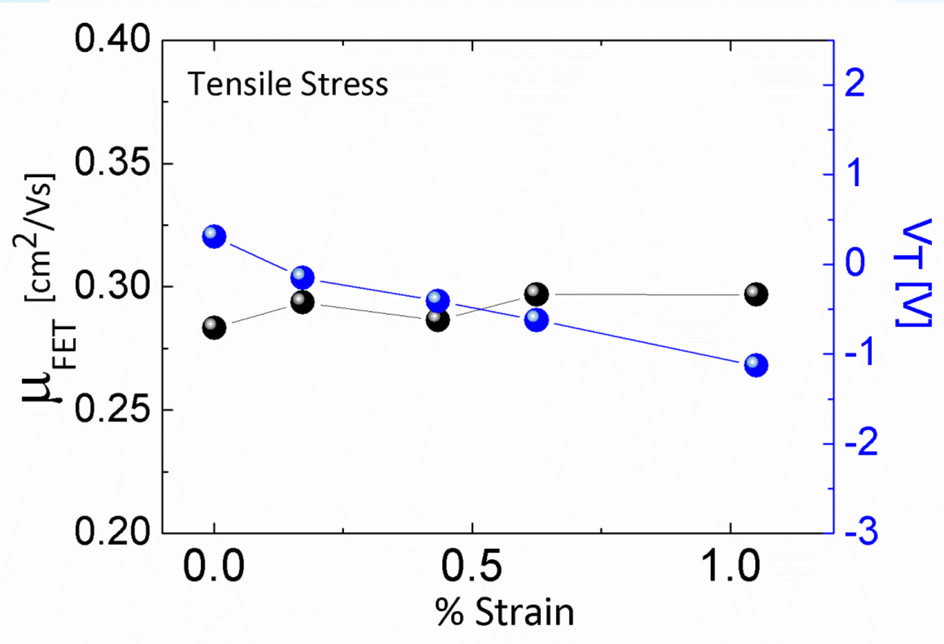


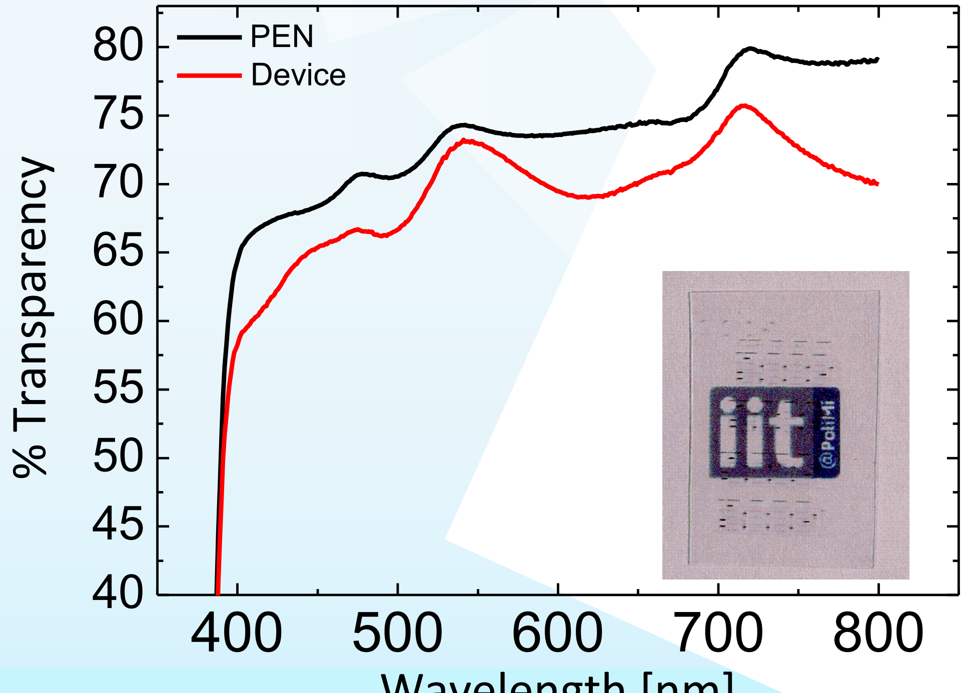


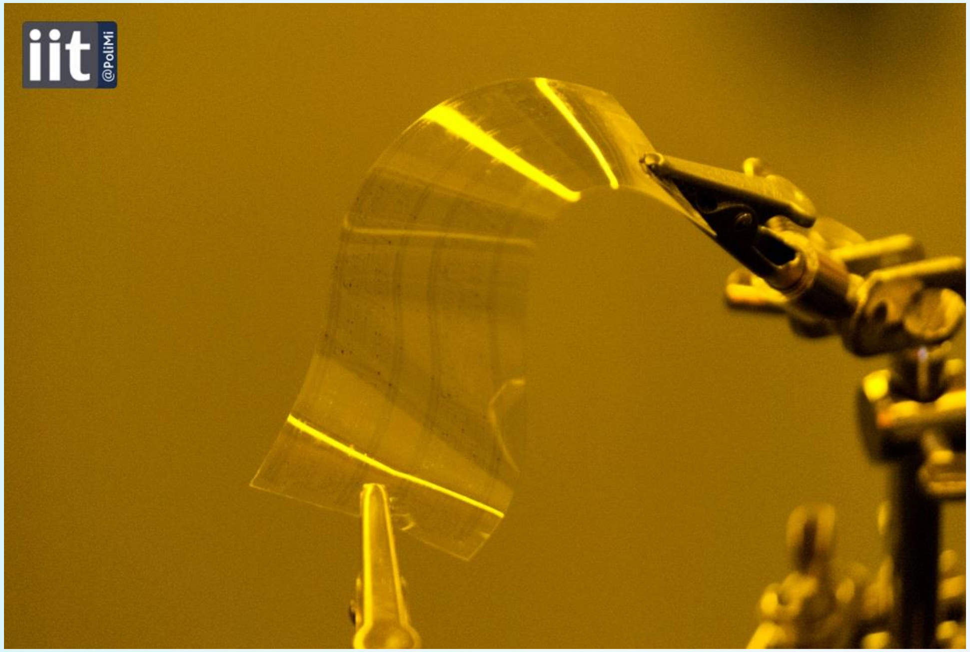
Bendability and Transparency

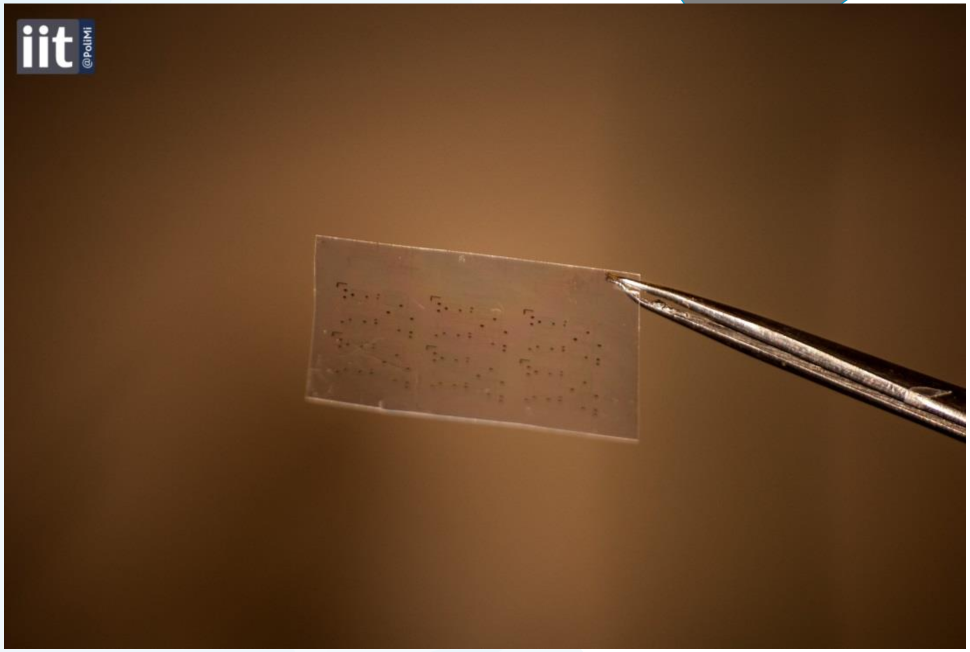


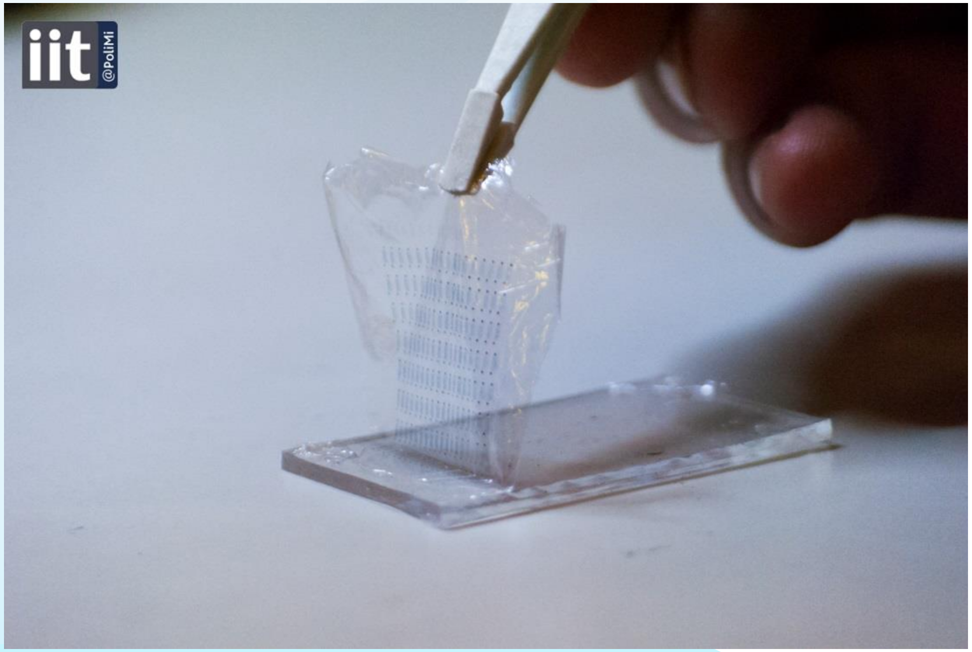






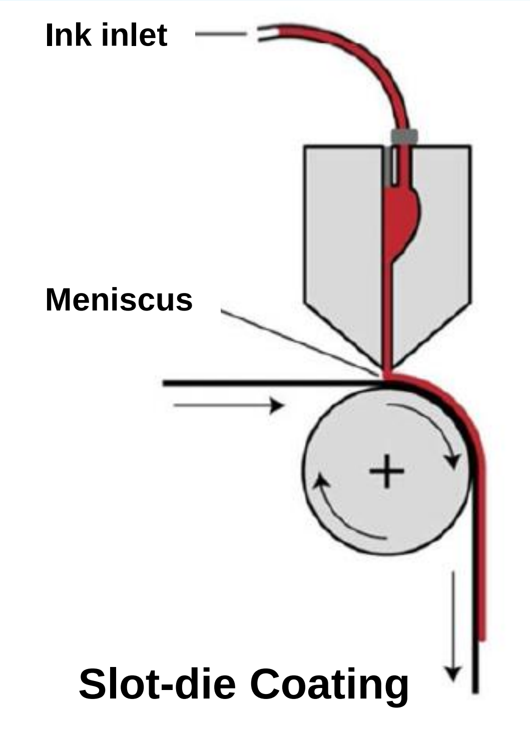






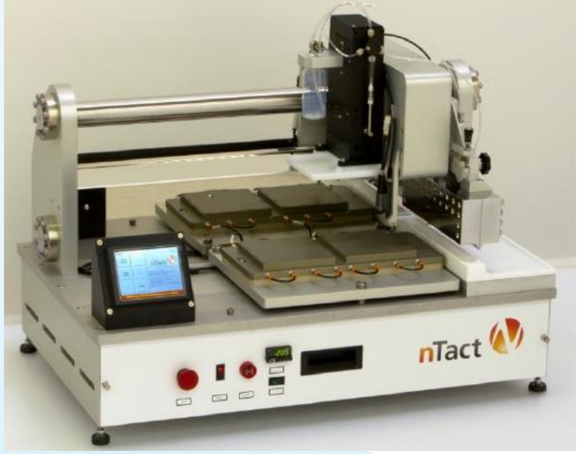
Process compatible with ultra-thin substrates
~ 1 μm

Slot-die coating



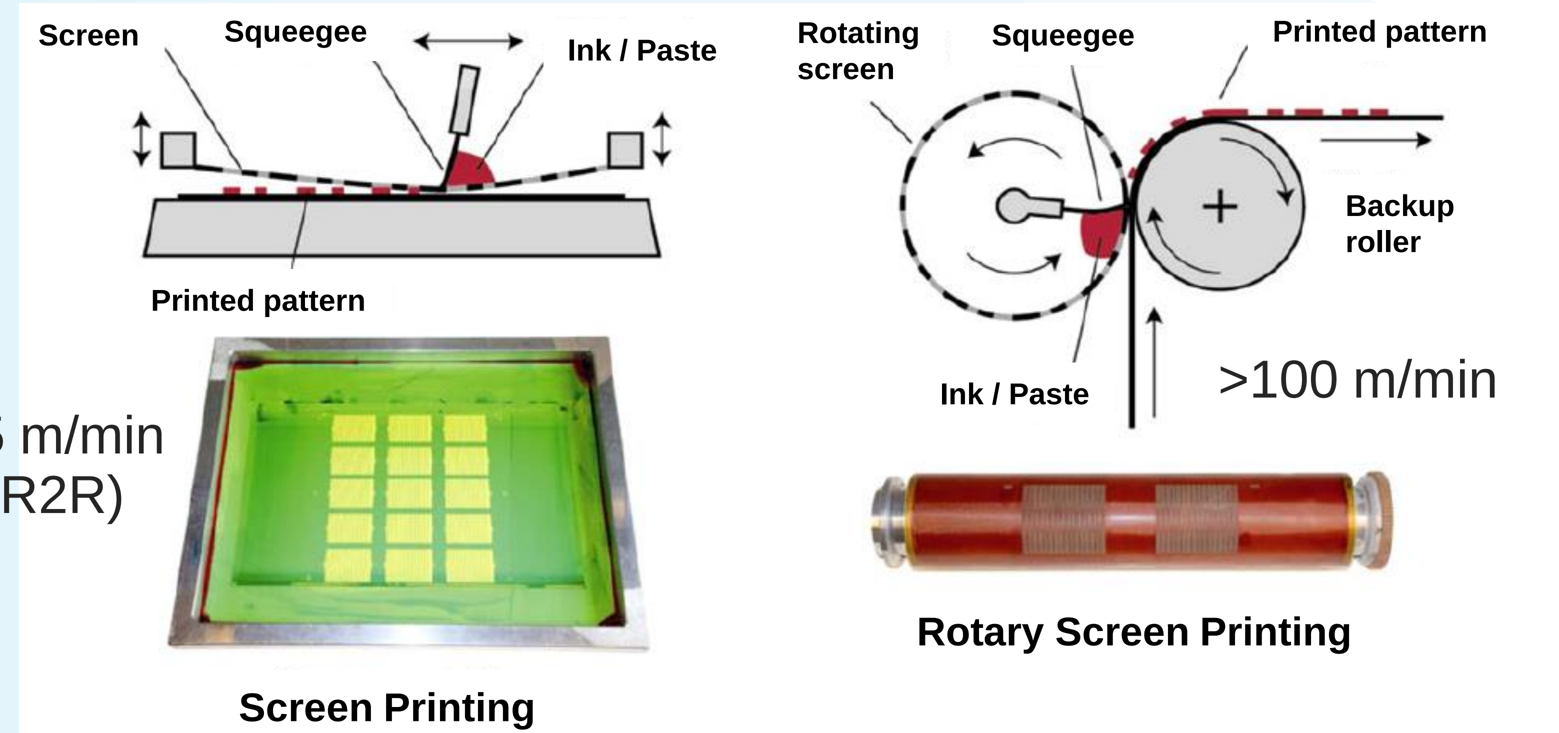
- Pre-metered coating (pumping speed, meniscus width, coating speed)
- Viscosity range: 1 – 1000 cps
- Very precise control of thickness from 100 μm down to 20 nm
- Uniformity 3 %
- Deposition of ink stripes
- Very low material waste
- Flat bed and R2R compatible

LIMITATIONS
- 0 to 1 dimensional patterning
- strong influence of process and fluid parameters



Krebs et al., JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS 2013, 51, 16–34

Screen Printing

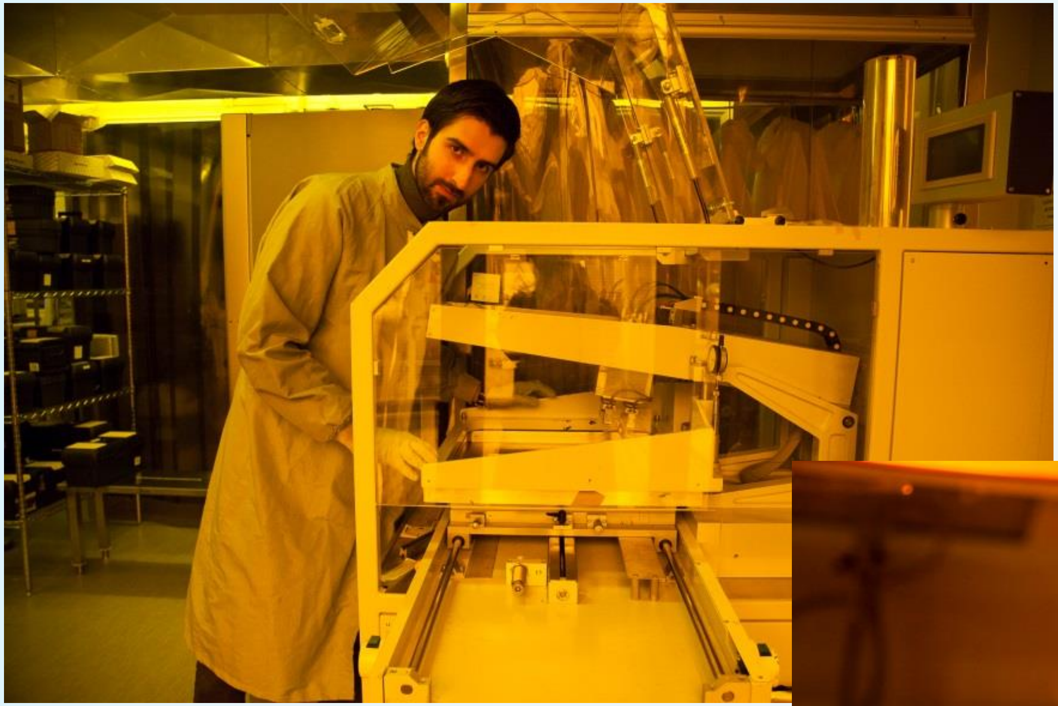


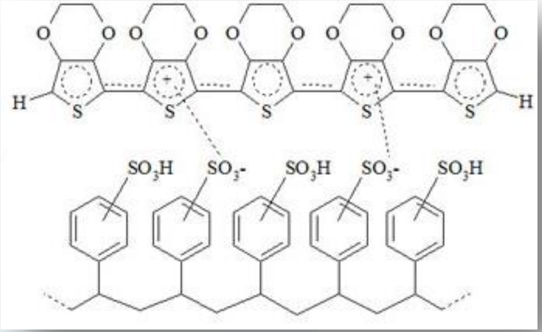
0–35 m/min (in R2R)

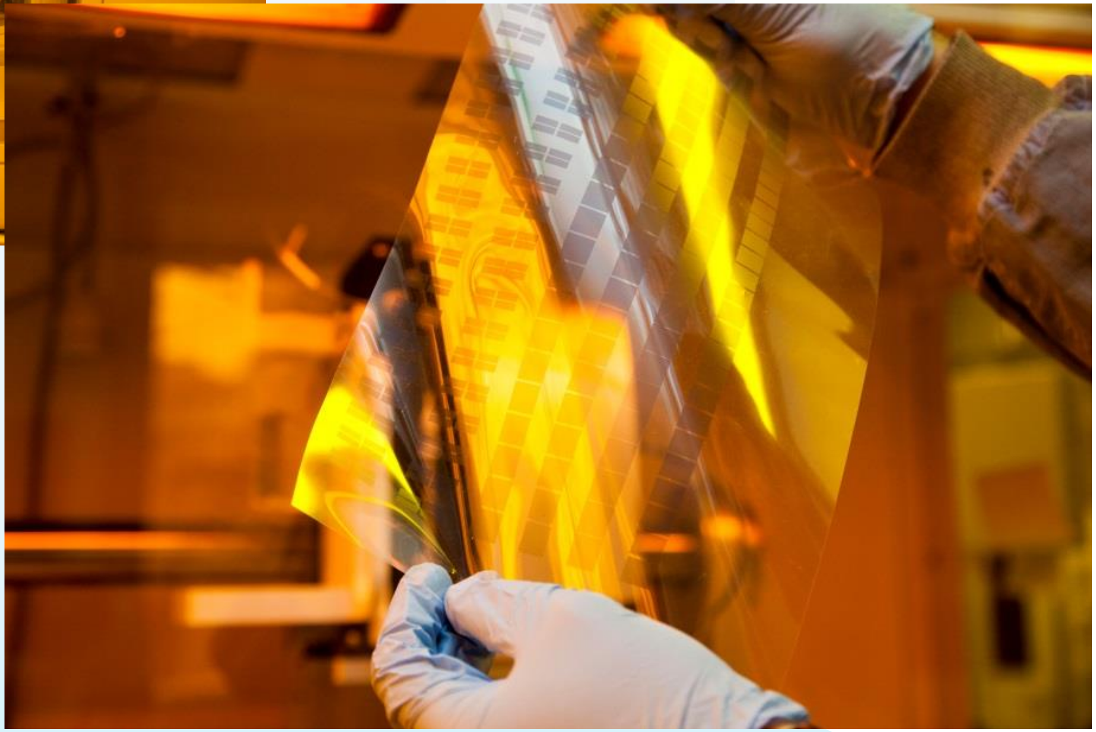
- Thick films
- High viscosity inks (> 1000 cps)
- Feature size 20 – 100 μm
- e.g. TiO_2 pastes for DSSCs

Krebs et al., JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS 2013, 51, 16–34

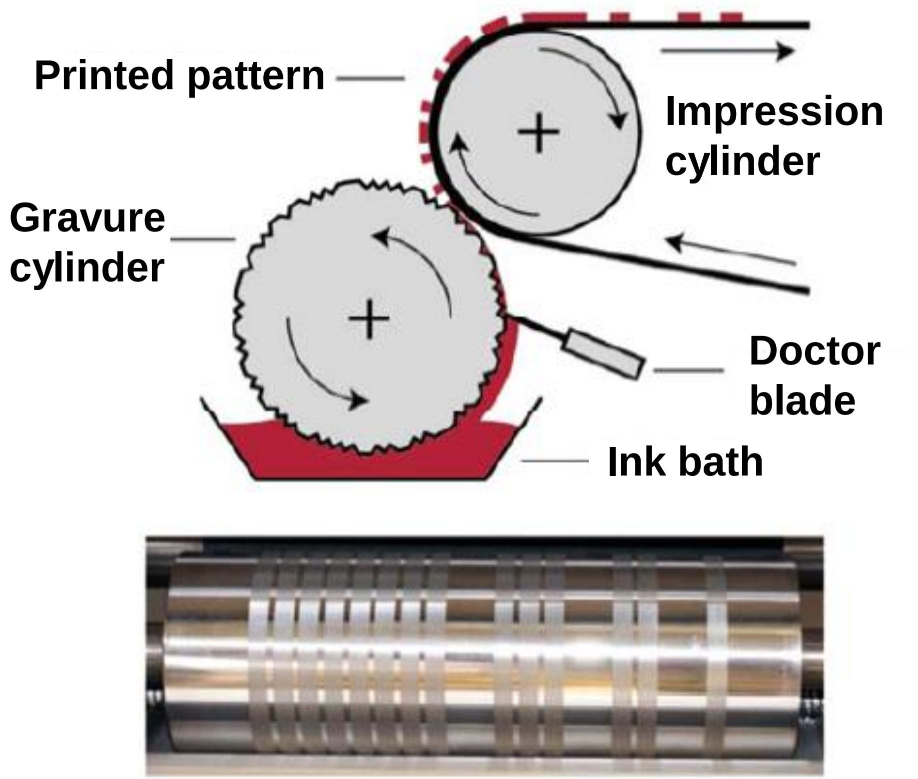
Printing Equipment







Gravure Printing



Gravure Printing

- 2D patterning
- Low viscosity inks (10 – 200 cps)
- Fast printing (15 m/s !)
- Feature size: < 100 μm

Limitations:
- expensive engraved rolls
- fine tuning of ink rheology

Krebs et al., JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS 2013, 51, 16–34

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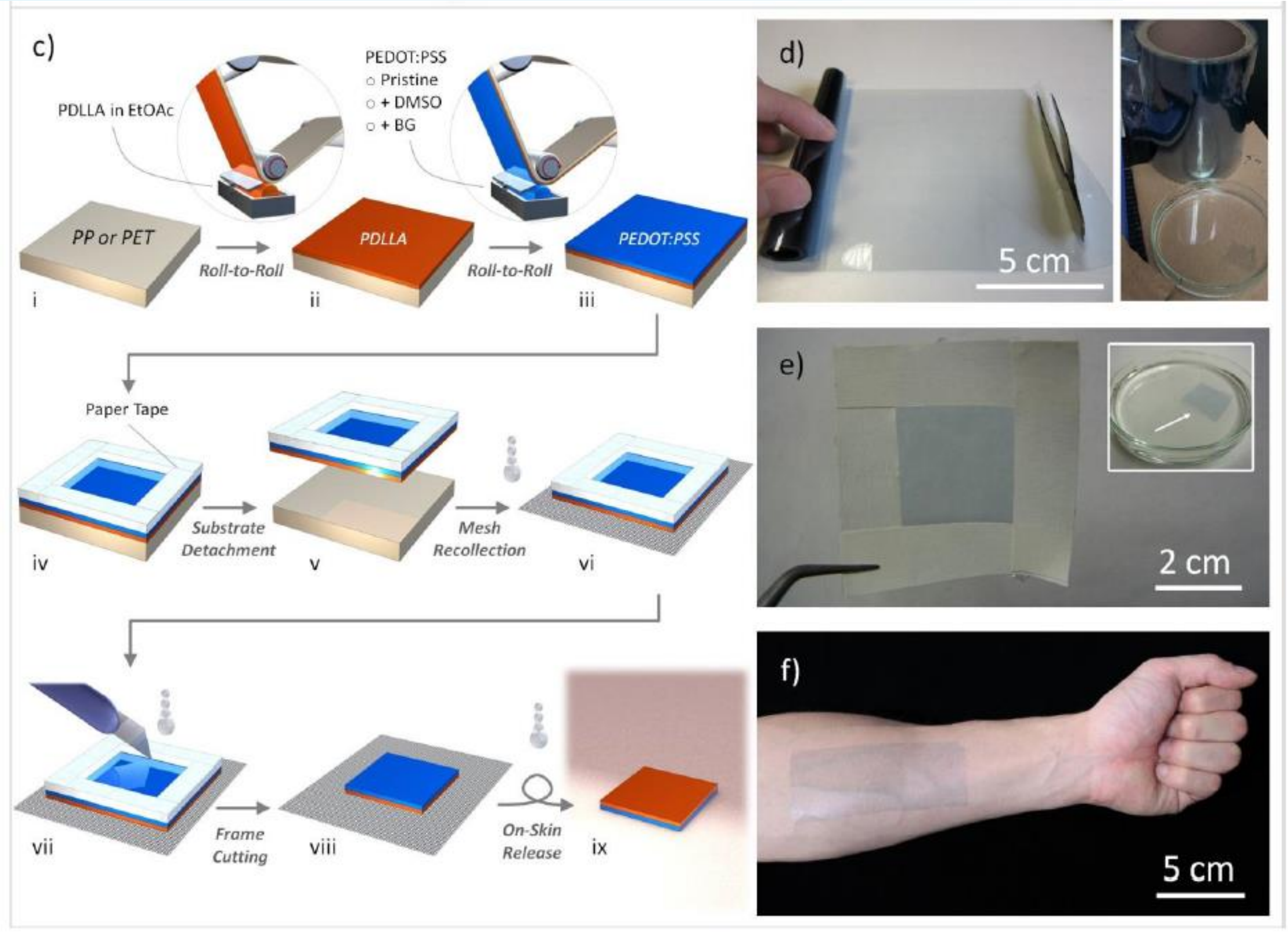
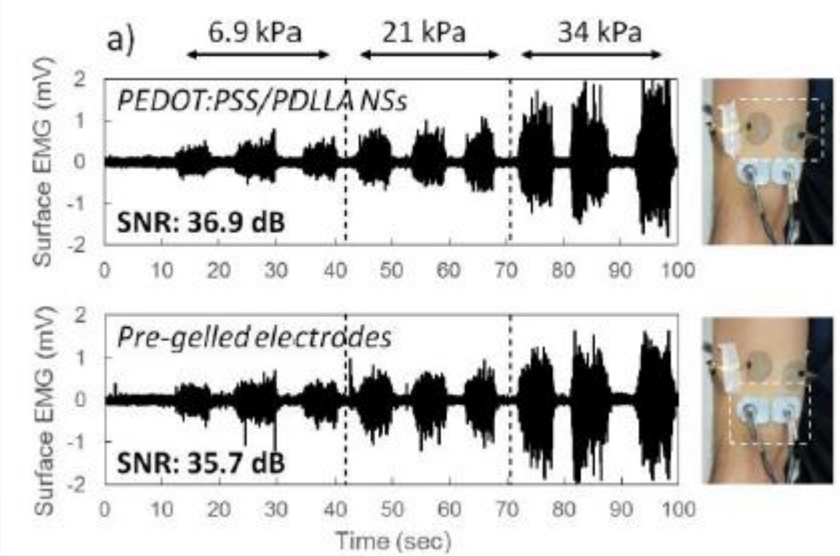
Gravure coated conductive tatoos



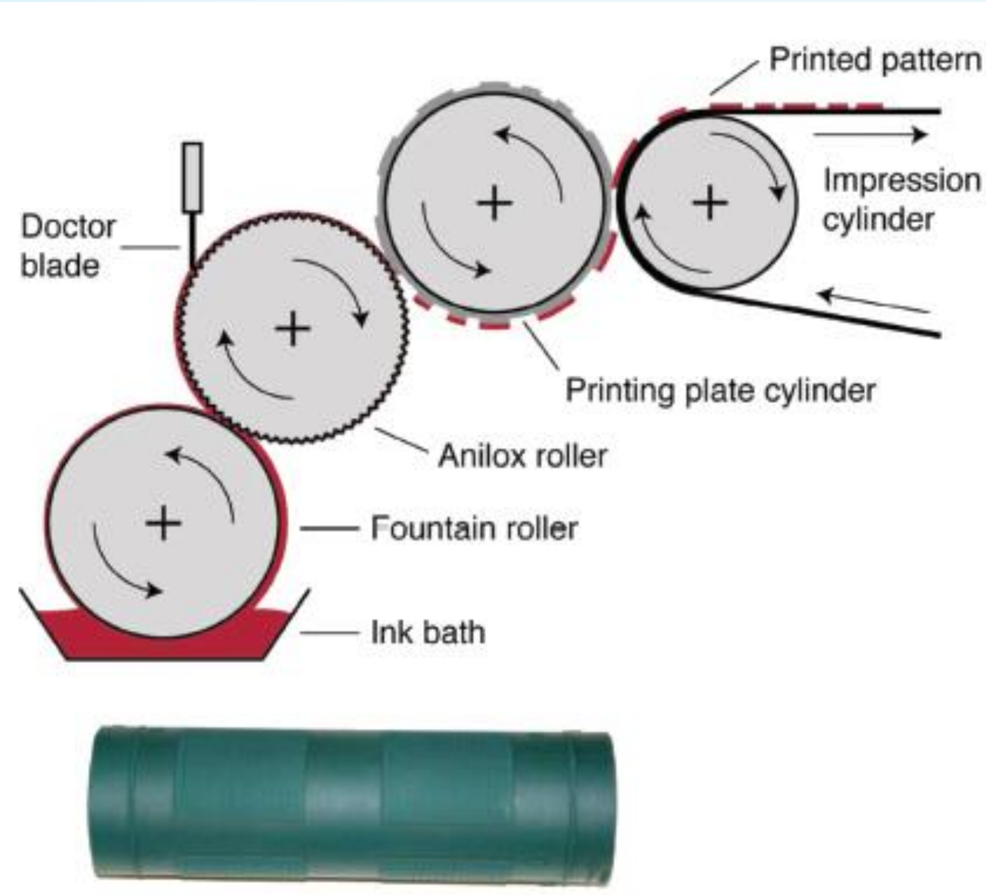
Francesco Greco, Virgilio Mattoli, IIT@SSSA, Pontedera

Gravure coated conductive tatoos



Francesco Greco, Virgilio Mattoli, IIT@SSSA, Pontedera

Flexography



- 2D patterning
- Low viscosity inks (50 – 1000 cps)
- Fast printing (10 - 15 m/s)
- Feature size: ~ 50 μm
- Cheap printing plates (photopolymer)
- Soft contact with the substrate (“kiss”)

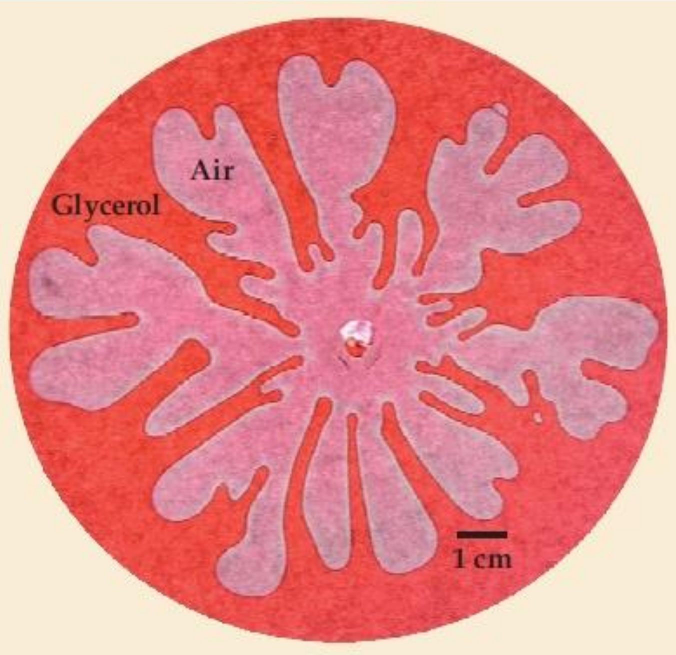
Limitations:

- solvent compatibility
- fine tuning of ink rheology

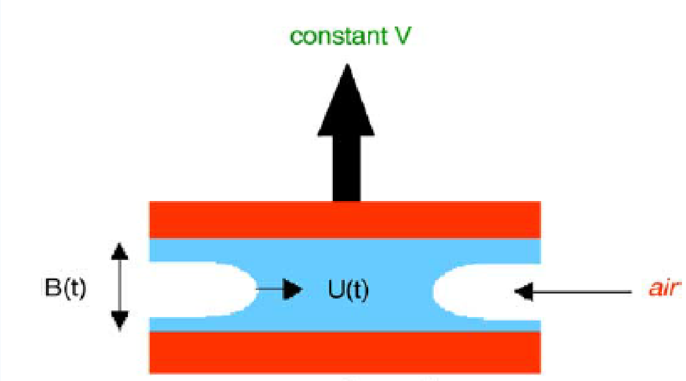
Krebs et al., JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS 2013, 51, 16–34

Viscous fingering

Instability occurring when a less viscous medium (e.g. air) rapidly displaces a more viscous medium



Wilson, Physics Today October 2012



“Hele-Shaw” cell

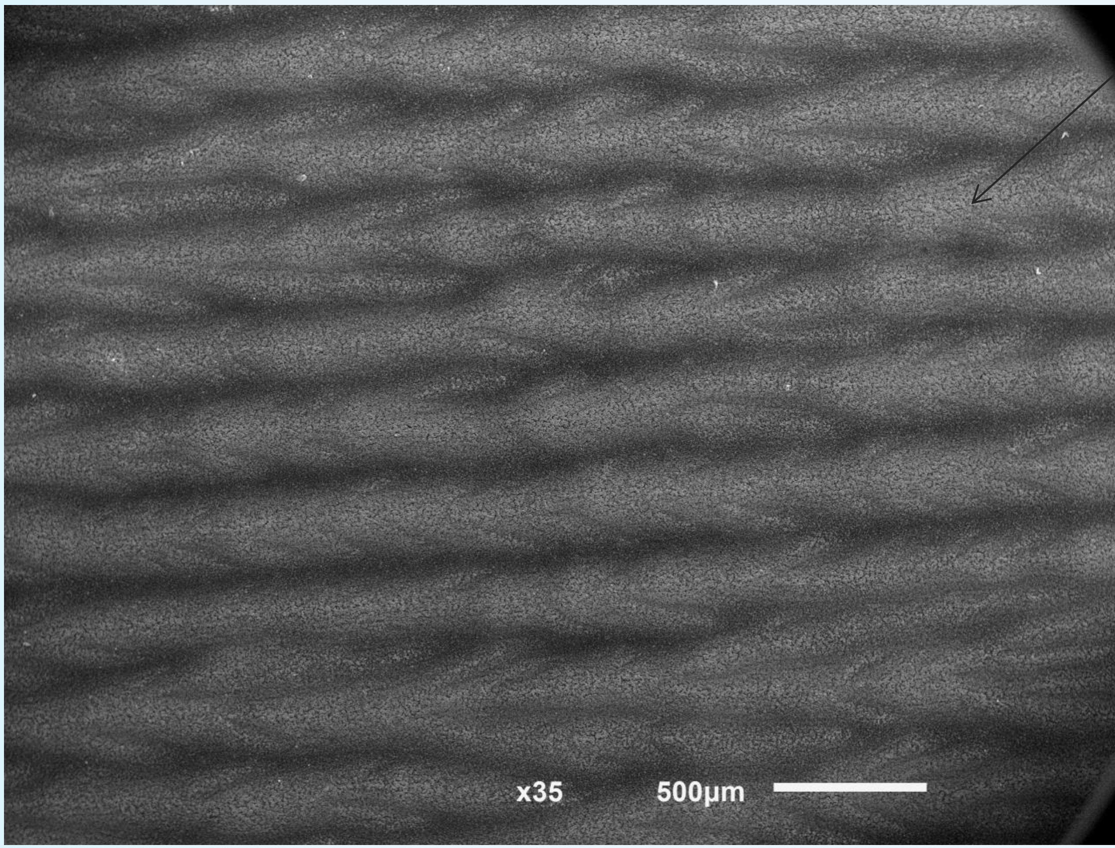
Amar et al., Physica D 209 (2005) 1–16

$$\Lambda = \pi \sqrt{\frac{\gamma h_{\mathrm{avg}}^2}{\eta V}}$$

Miller et al. J. Vac. Sci. Technol. B 20.6., 2002

Flexo printed Ag on PET

Fingers height ≈ 500 nm



printing direction

low volumes (3.3 cm^3/m^2)

larger finger-pitch

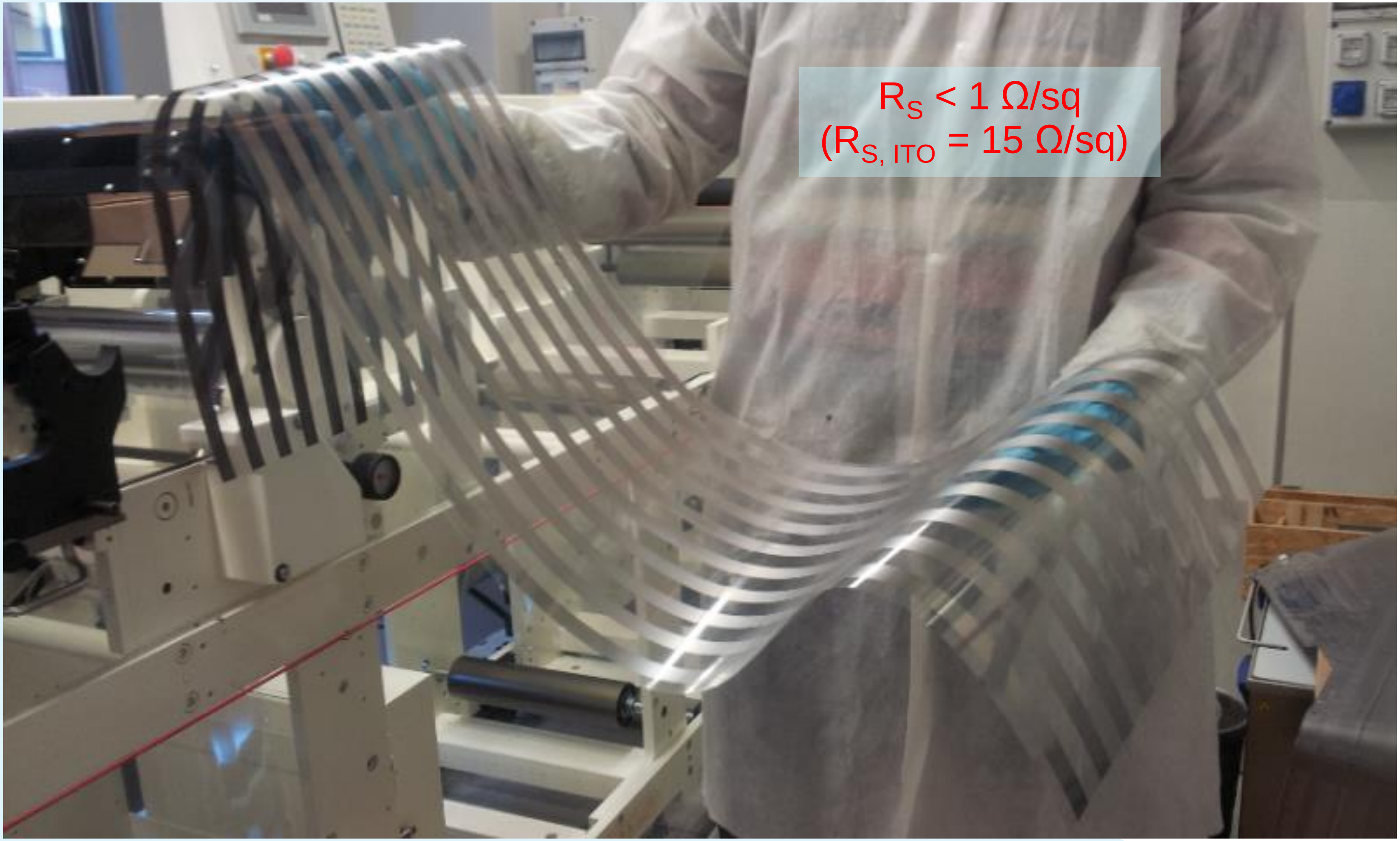
lower resistivity

high volumes (21.5 cm^3/m^2)

$$\Lambda = \pi \sqrt{\frac{\gamma h_{avg}^2}{\eta V}}$$

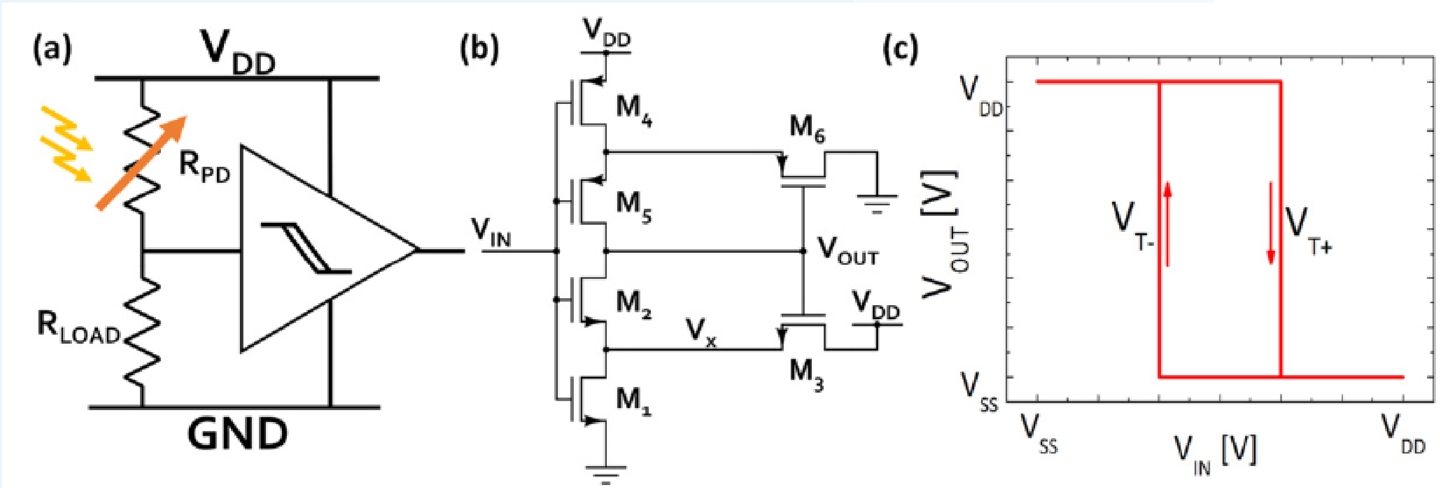
Miller et al. J. Vac. Sci. Technol. B 20.6., 2002

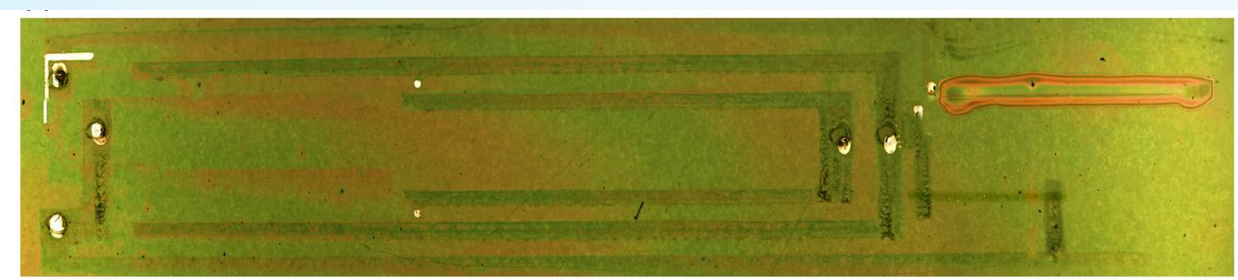
Flexo printed Ag on PET

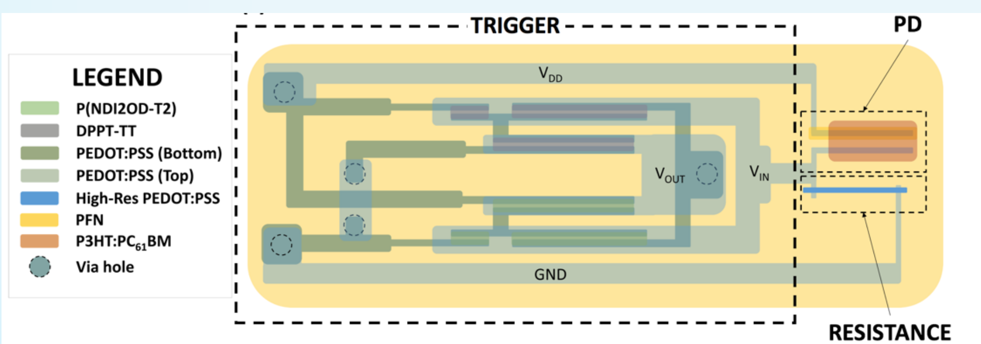


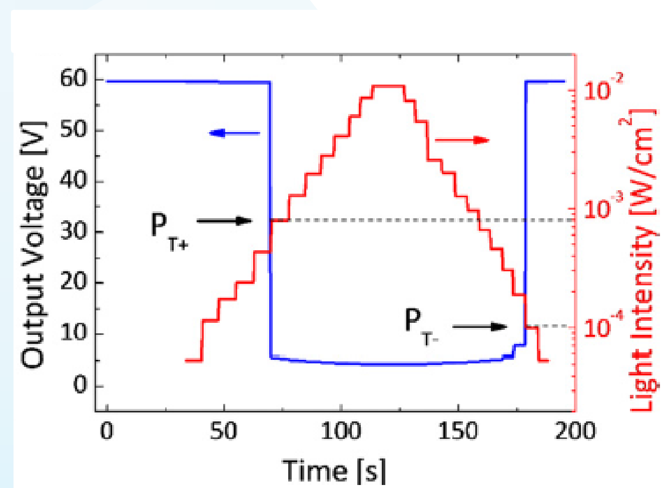
R_S < 1 Ω/sq
($R_{S, ITO}$ = 15 Ω/sq)

Integrated Plastic Systems









Semicond. Sci. Technol. 30 (2015) 104005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