Physics of printing – a multi-scale approach

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idd printing science technology

Overview

- Functional printing research at the IDD @ TU Darmstadt

- Inkjet & Gravure printing - sequences of physical processes:
  fluid dynamics – wetting & capillarity – evaporation – phase transitions

- Printed layer & pattern formation on macroscopic, mesoscopic, and molecular length (and time) scales.
  Capillary surface leveling – Solvent evaporation – Marangoni drag

- Examples of printed organic semiconductor layers

- Conclusion

The Institute of Printing Science and Technology (idd)

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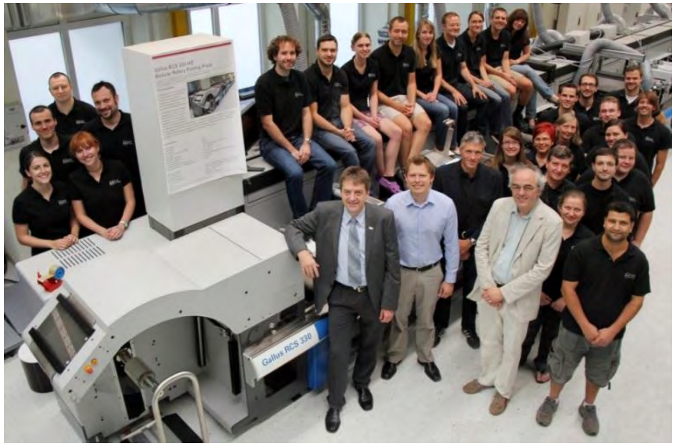
- Founded in 1953 as a research institute by leading German printing press manufacturers
- Part of the Department of Mechanical Engineering,
  Darmstadt University of Technology
- 28 employees (3 senior researchers, 15 PhD students, 3 printing engineers)

„Make printing more industrial"

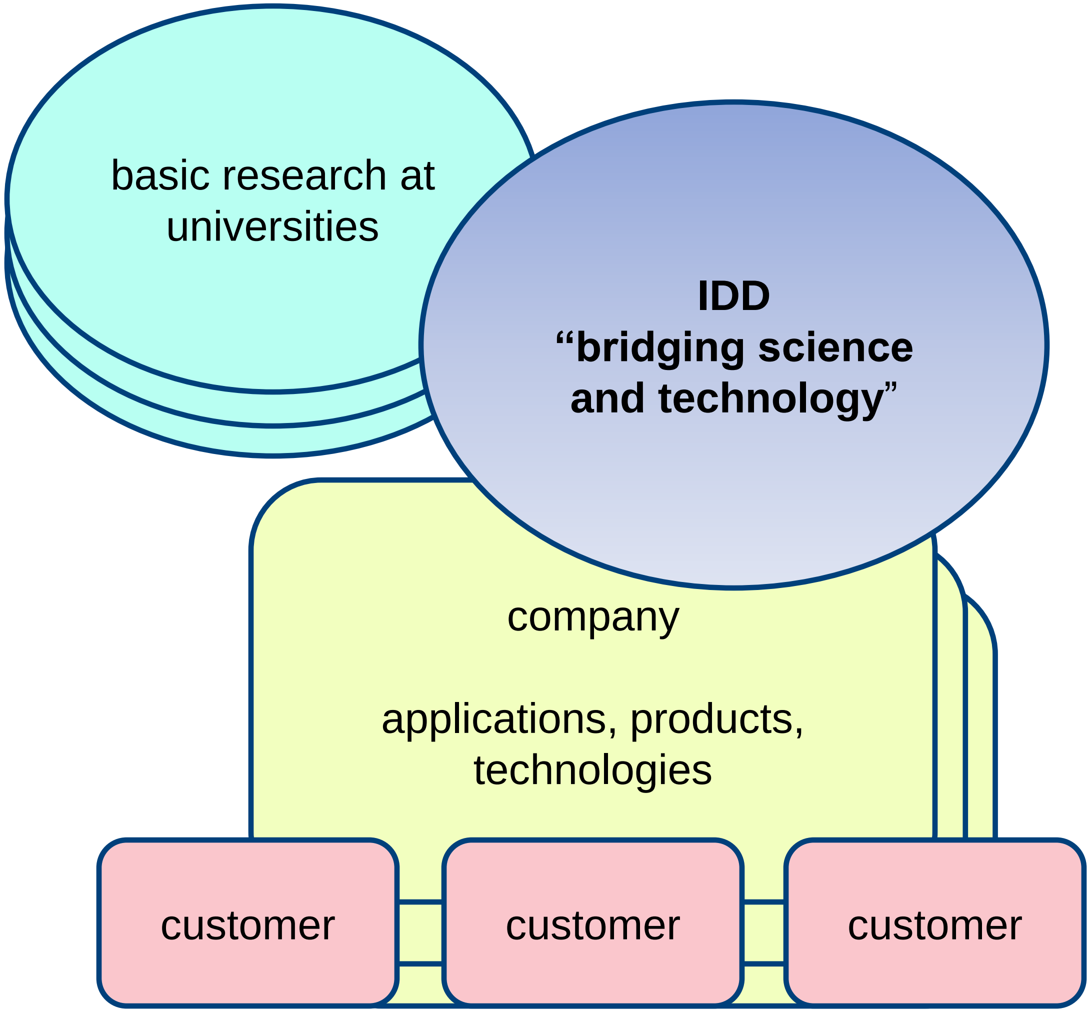
Source: IDD



Research groups & topics:

- Color Science
- Automatization and measurement
- Functional printing

Printing Science and Technology at IDD



basic research at universities

IDD
“bridging science and technology”

company

applications, products, technologies

customer

customer

customer

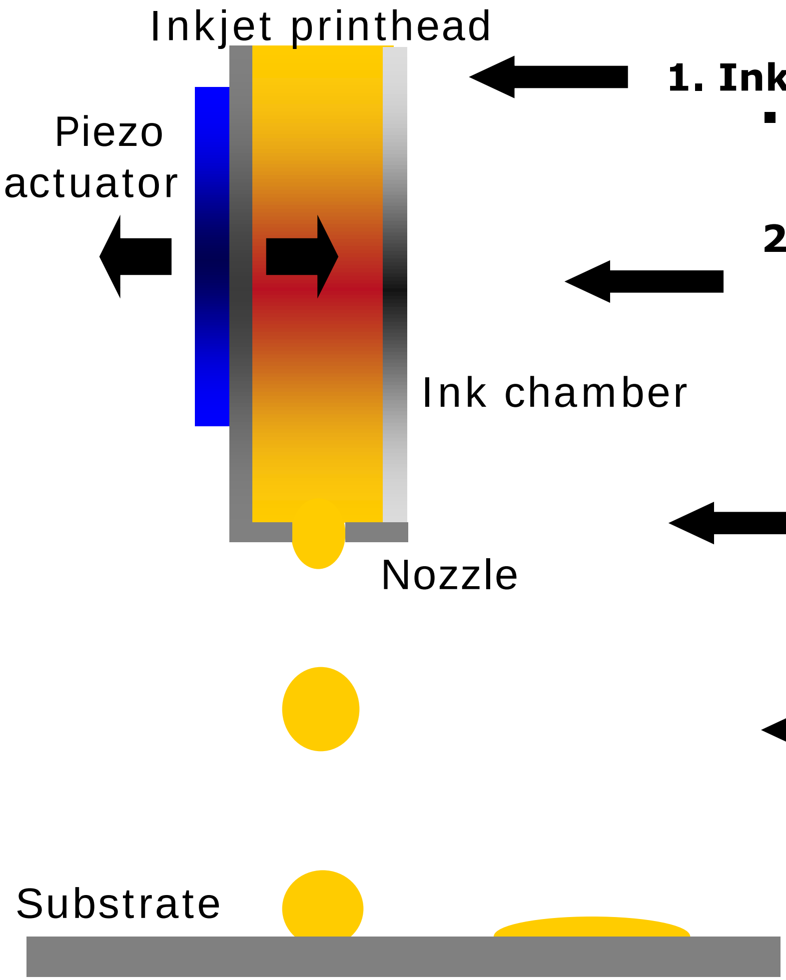
Concept of Research:

- ➢ characterization and modelling of printing
- ➢ developing measurement methods
- ➢ derive concepts for industrial production

Functional printing fluids - examples

Fluid preparation	Example	Typ. concen-trations (wt.-%)	Typ. viscosity (mPa s)	Preferred printing technique
Solution	Small-molecule dyes/semiconductors in toluene	< 5	0.8 - 3	inkjet, gravure
Polymer solution / dispersion	Polymer semiconductors in toluene	< 10	1 – 200	inkjet, gravure, flexo
Colloidal dispersion	Nano-silver in organic solvent	< 5	1 – 200	Inkjet, gravure, flexo
Suspension	Conductive silver ink	10 - 70	200 - 10000	Screen-, pad-printing

Inkjet printing



1. Ink acquisition

- ink supply from the reservoir

2. Pre-dosing of fluid

- Piezo actuator creates an accoustic pressure wave inside the chamber, running towards the nozzle

3. Dosing of the printing fluid

- The accoustic wave is transformed to an accelerating fluid fliament extruding through the nozzle.

4. Ink transfer to the substrate

- The fluid flament releases a drop of defined volume and velocity.

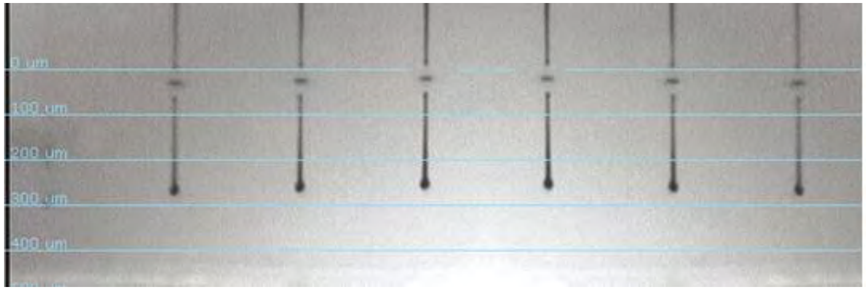
5. Fluid dynamics on the substrate & solidification

Inkjet Printing @ IDD

- Printheads:
  - DMC-11601 – 1pl drops
  - DMC-11610 – 10pl drops
  - 16 nozzles are arranged in 1 row

- Frequency: 1 kHz - 20 kHz

- Wave form control
- Drop formation control
- Drop volume control



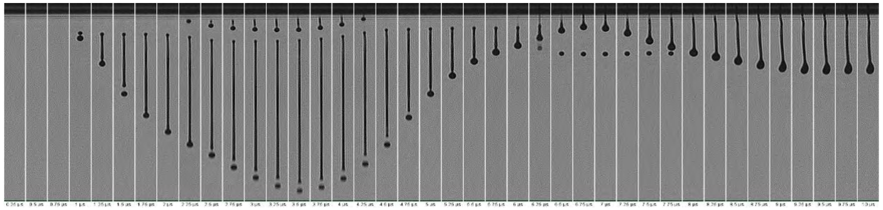
Dimatix FUJIFILM ™

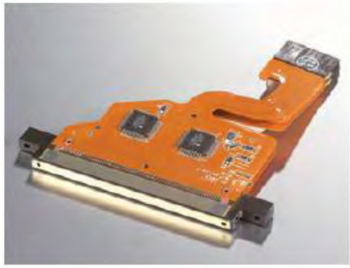
Inkjet Printing @ IDD

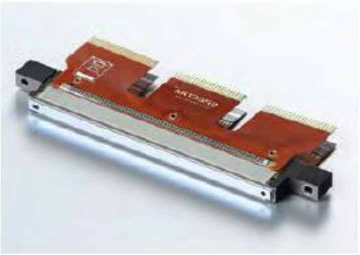
- Printheads:
    - S-Class
    - Spectra SE3, SX3
    - Xaar 1001

- Frequency: 1 Hz - 20 kHz in 1 Hz steps

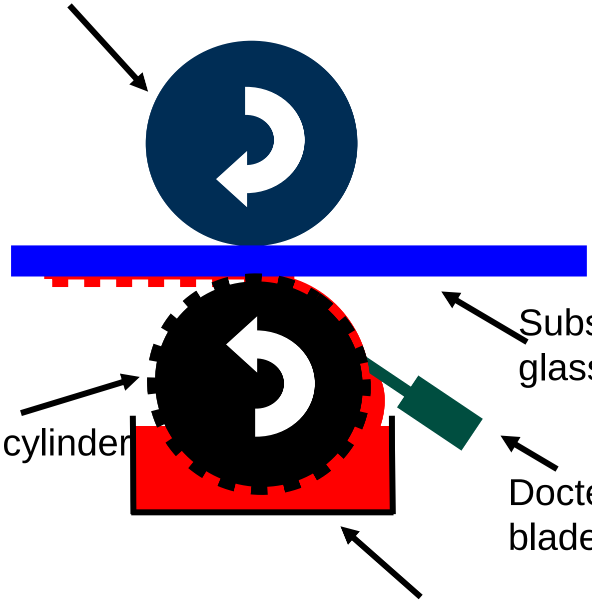
- Wave form control
- Drop formation control
- Drop volume control




S-class


Spectra SE, Spectra SX3

Gravure printing – the principle



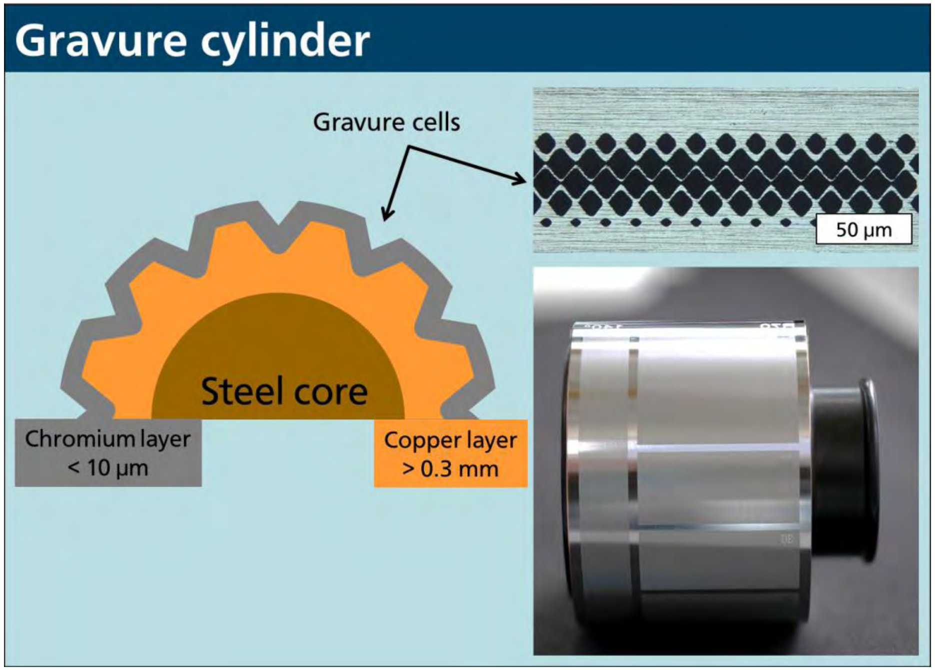
Impression cylinder

Substrate: glass, foil

Gravure cylinder

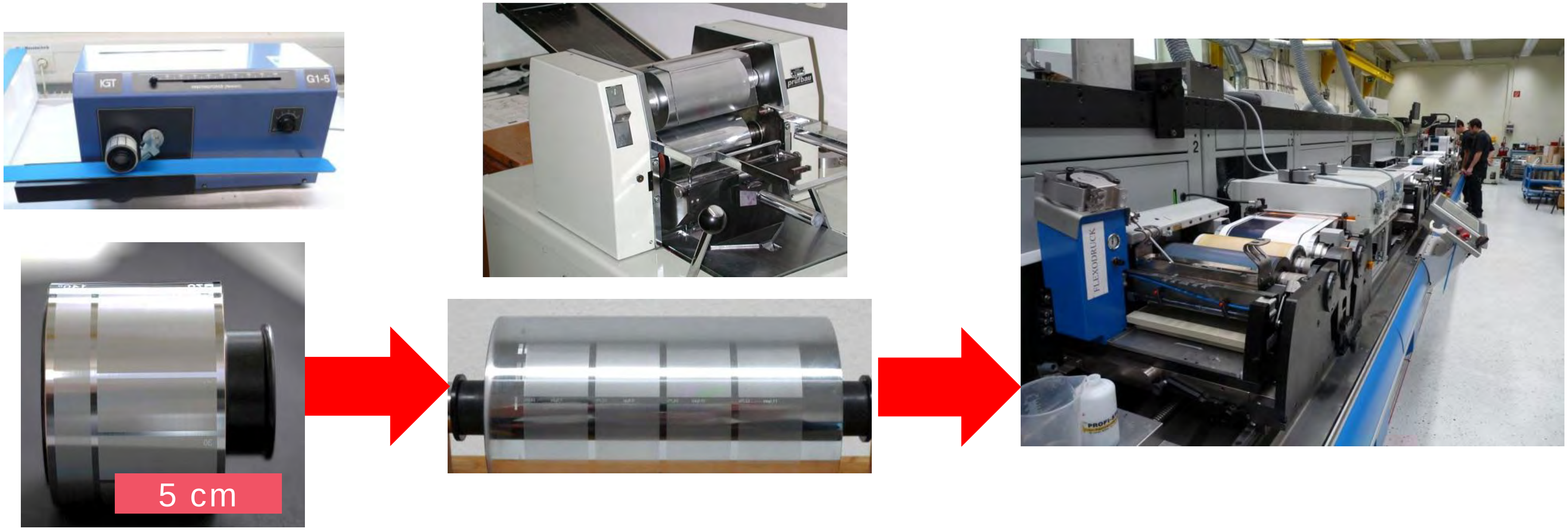
Docter blade

Fluid reservoir



- Inkjet & gravure printing fluids have very simillar viscosity, surface tension
- One (almost) always can do both techniques with the same fluid

From Lab to Fab: gravure @ IDD



Scale	Printability test	Lab printer	Production scale
Output	20 cm^2/run	500 cm^2/run	50 m^2/min
Ink consumption	1 ml/run	20 ml/run	5 l/h (per unit)
Printing speed	0.1 – 1 m/s	1 – 5 m/s	1 – 3 (- 16) m/s

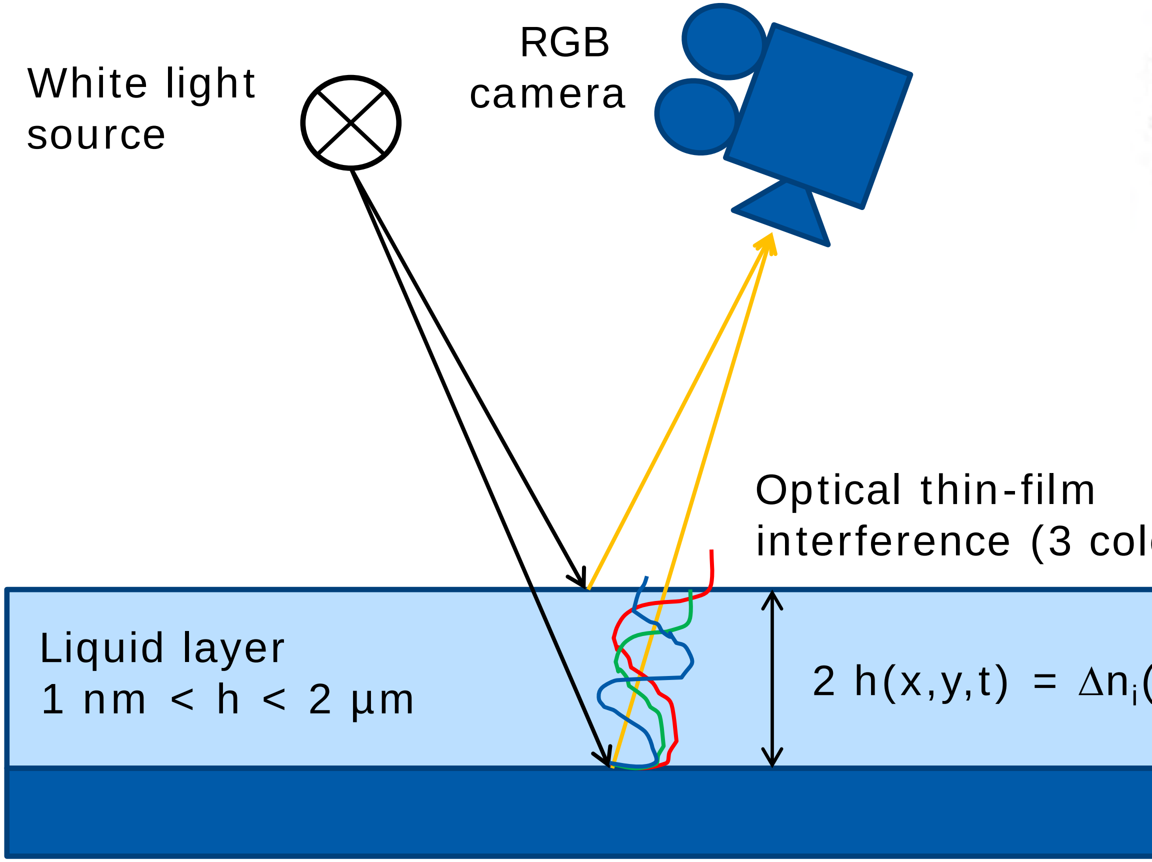
Gravure printers – new developments

- New machine concept by IDD, Prüfbau GmbH, Heidelberger Druckmaschinen AG
- 15 x 15 cm gravure & flexo lab printer
- using volatile solvents (toluene, MEK, THF,…)
- Printing under N_2/Ar
- … and under saturated solvent vapor atmosphere
- Fully encapsulated and explosion protected
- Glass and foil substrates
- Glove-box-compatible substrate handling

Printing - a sequence of physical processes

	Inkjet (DOD)	**gravure**
Conditioning of the printing fluid	Ink supply for printhead	Ink flow dynamics in the reservoir
Fluid acquisition by the printing unit	Pressure control at the ink inlet of the printhead, acoustic wave suppression	Ink entrainment into / air expulsion from gravure cells
Metering / predosing of the printing fluid	Piezo actuator operation & acoustic wave propagation	Doctor blading / ink flow & shear on the gravure cylinder surface
Dosing of fluid according to the printing pattern	Printhead nozzle: fluid acceleration / filament formation by acoustic waves	
Fluid transfer to the substrate	Fluid filament breakdown & drop formation dynamics	Ink splitting at the nip, emptying of gravure cells
Fluid relaxation on the substrate	Capillarity-related drop coalescence on the substrate surface & solvent evaporation	
Solidification (Phase separation)	Crystallization from saturated solution / gelation	
Drying (removing solvent residuals)	Solid-state diffusion of solvent molecules	

Visualising nm-thin printed layer dynamics by inline color reflectometry (ICR)



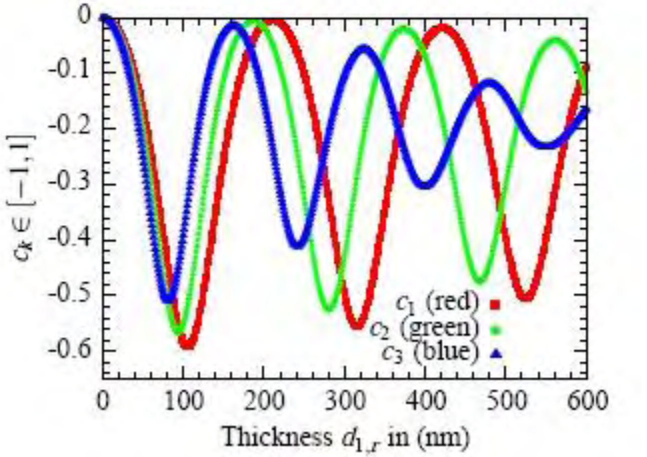
White light source

RGB camera

Optical thin-film interference (3 color channels)

Liquid layer
1 nm < h < 2 µm

$2\ h(x,y,t)\ =\ \Delta n_i(x,y,t)\ \lambda_i$



RGB color contrast of a SiO_2 layer

From: Bornemann & Dörsam 2014

Printing = fluid transfer + solvent evaporation + solid layer formation

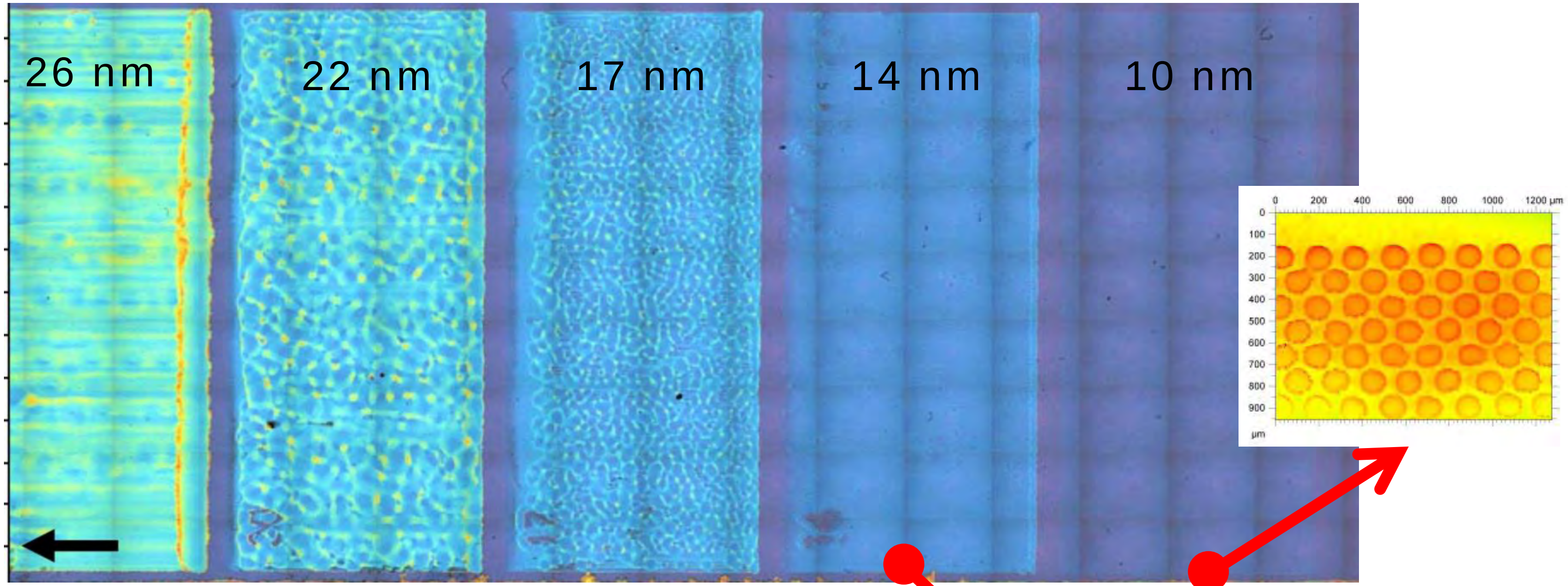
Gravure printed OLED layers

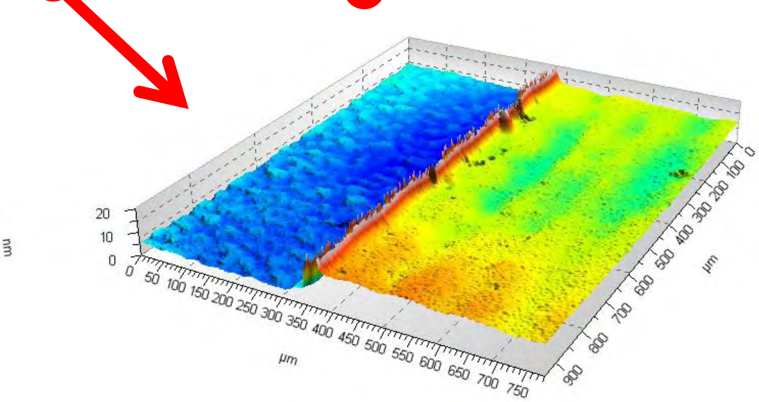
Film splitting, Ribbing, fingering

Film splitting ? Isotropic finger instability

Functional, homogenous layer

Dot ink splitting

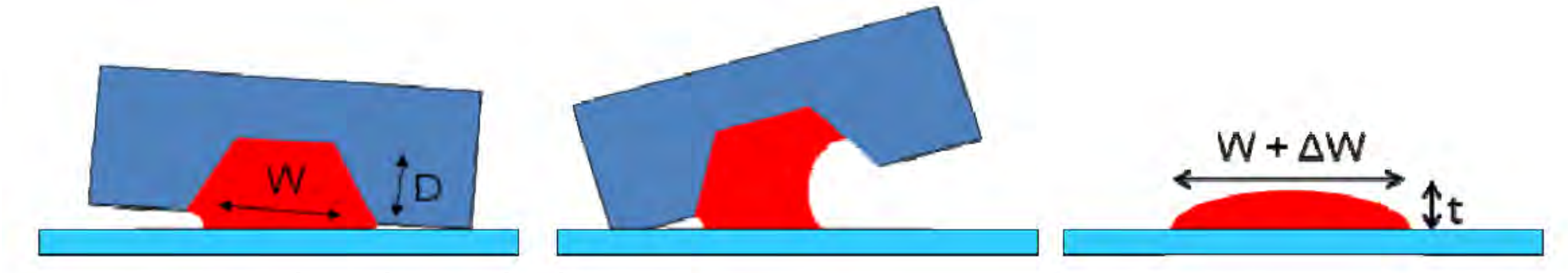




ICR profile of a semiconductor printed as toluene solution, on ITO glass.

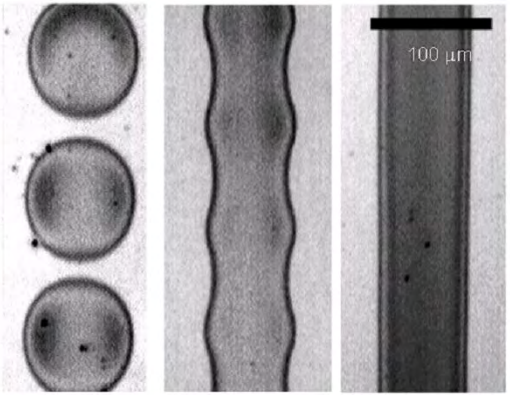
From: Bornemann, Sauer & Dörsam 2011

Fluid dynamics on the substrate – drop coalescing by capillarity



Picture: Sung, master thesis, Berkeley, 2008

After cell emptying through dot ink splitting the droplets should coalesce to form uniform structures or layers.



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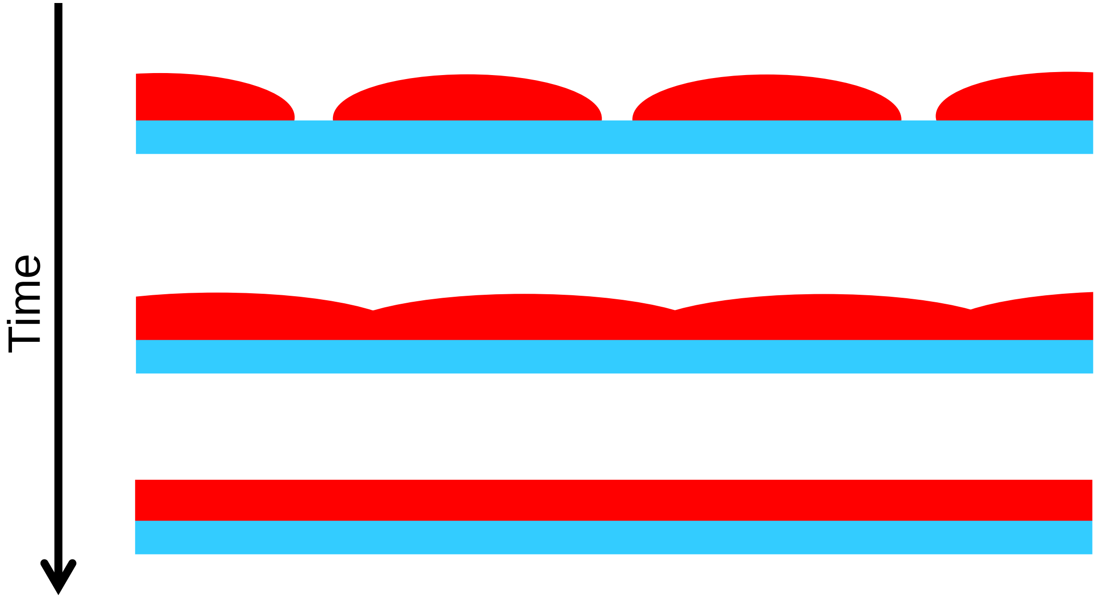
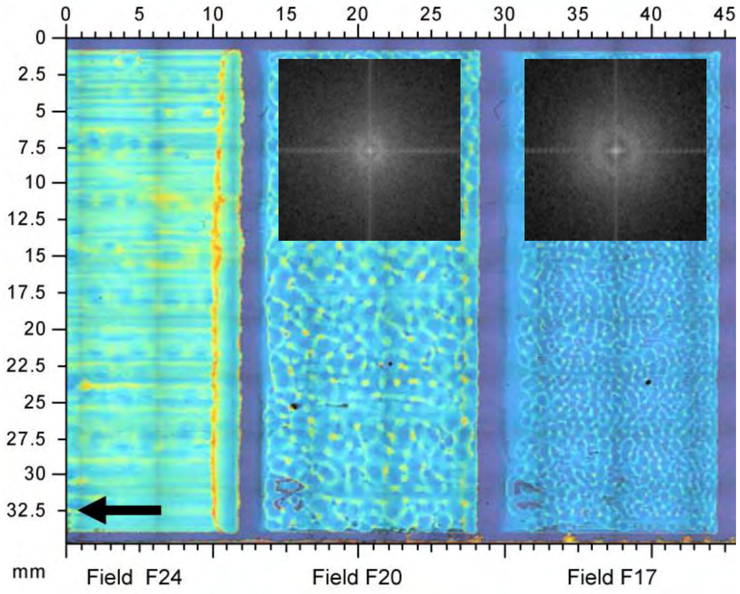
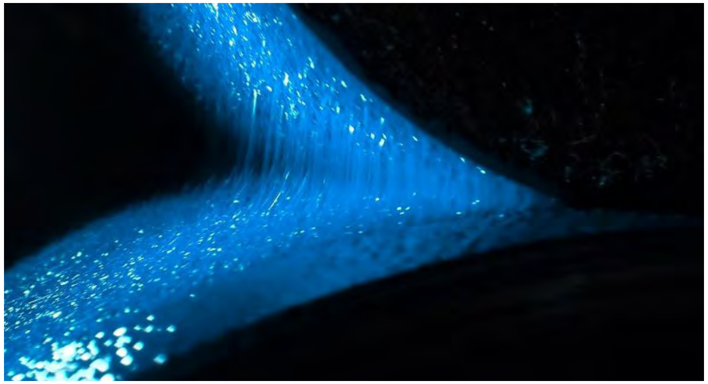


Pictures: IDD

Printing process: 4. Fluid dynamics on the substrate – leveling of undulations





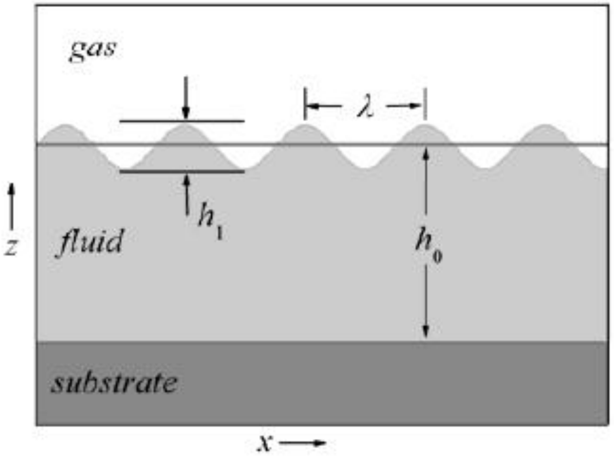
mm … cm

Leveling time of surface patterns: $$\tau_{lev} = \frac{3\eta\lambda^4}{16\pi^4\sigma h^3}$$

nm

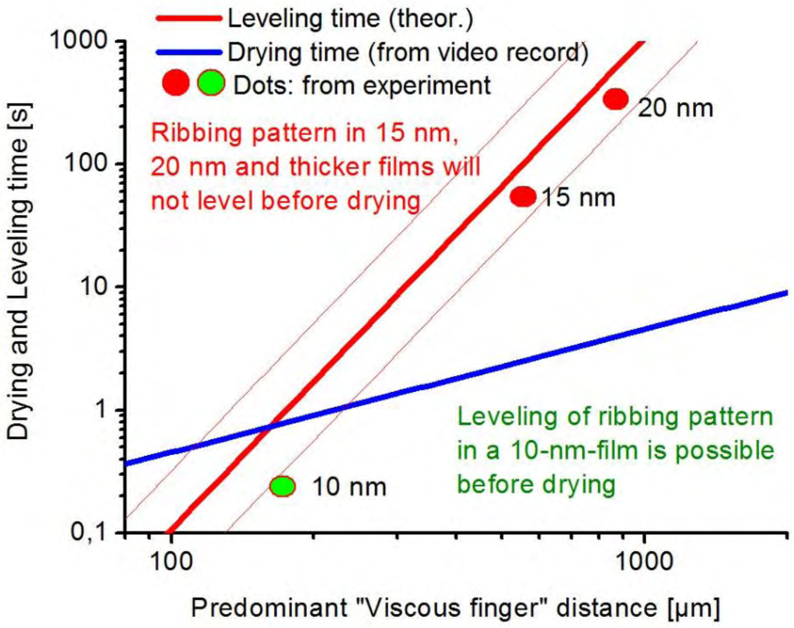
Parameters determined for printed fields F14 – F20.			
Field	**F14**	**F17**	**F20**
Dry film thickness h_d	10.5 nm	14.98 nm	19.98 nm
Wet film thickness h	0.39 µm	0.6 µm	0.8 µm
Dominant wavelength $\lambda_{F..}$	0.143 mm	0.73 mm	1.17 mm
Drying time τ_d	**0.76 s**	**1.84 s**	**3.08 s**
Leveling time τ_{lev}	**0.35 s**	**70 s**	**400 s**

Leveling vs. drying time



$$\tau_{lev} = \frac{3\eta\lambda^4}{16\pi^4\sigma h_0^3}$$

Landau & Levich 1942



N.Bornemann et al., JIST (2011)

Marangoni effect in printed liquid films

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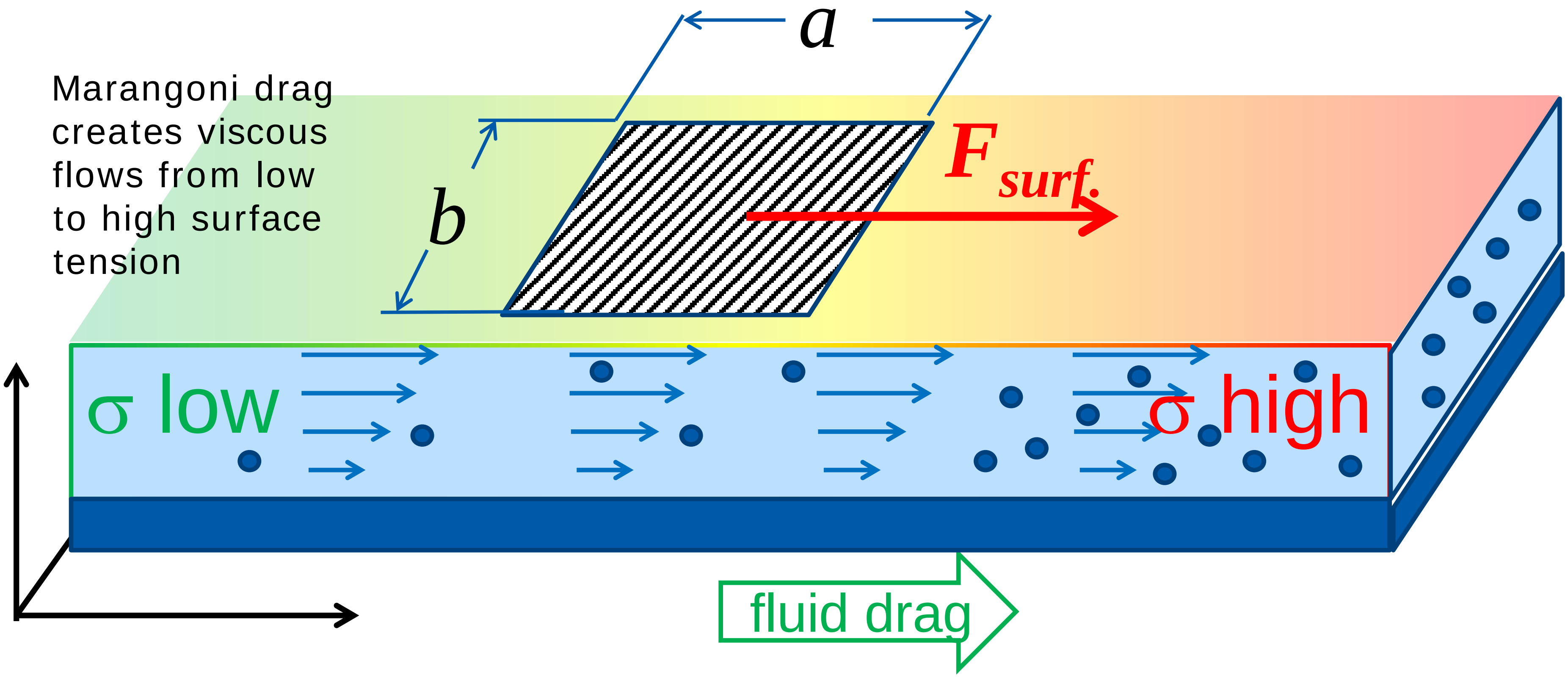
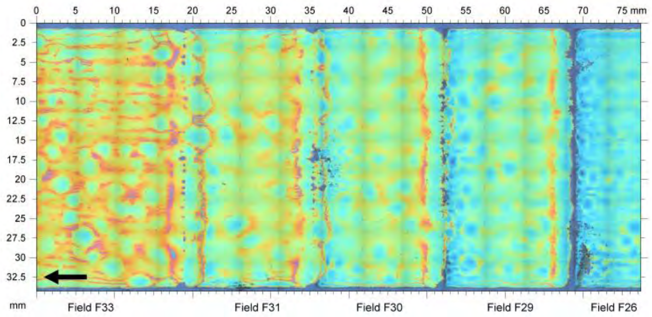
$$\vec{F}_{surf.} = a\,b\,\vec{\nabla}\sigma(T,C,\ldots) = a\,b\left(\left.\frac{\partial\sigma}{\partial T}\right|_{C}\vec{\nabla}T + \left.\frac{\partial\sigma}{\partial C}\right|_{T}\vec{\nabla}C + \ldots\right)$$

Marangoni drag creates viscous flows from low to high surface tension

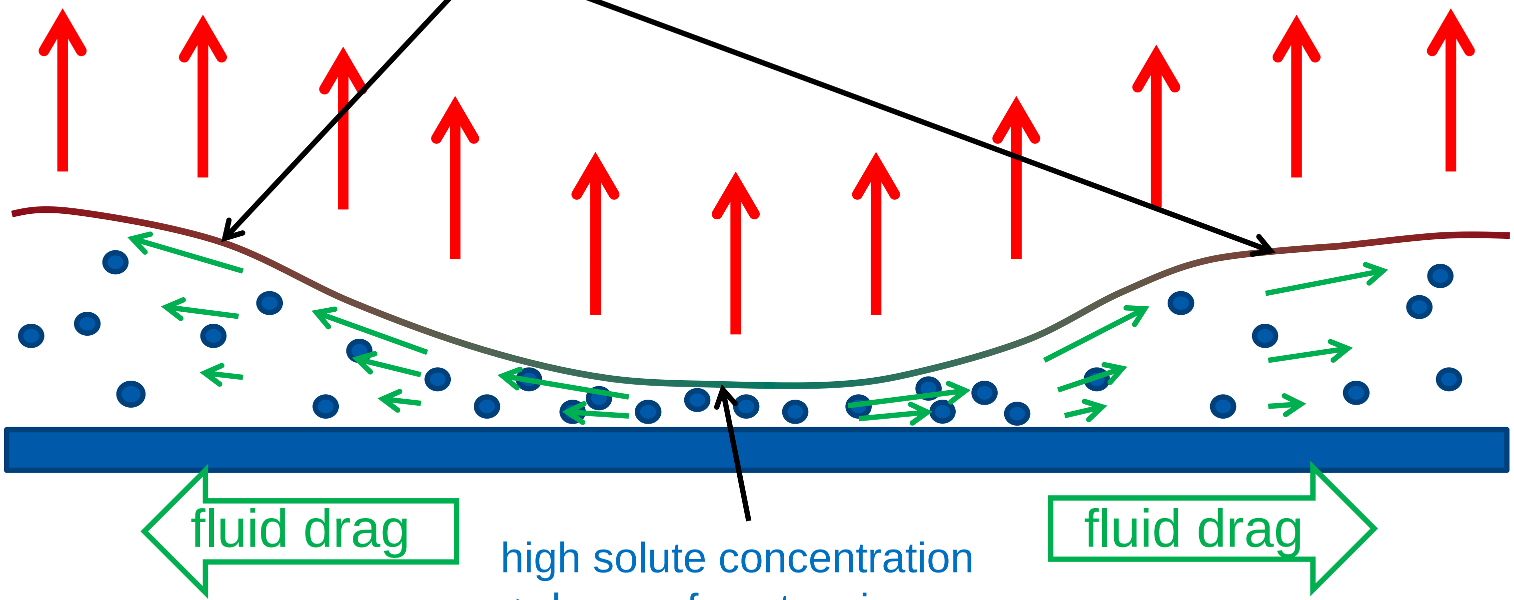


Pattern formation by Marangoni effect

$$\left(\frac{\partial\sigma}{\partial C}\right)_T < 0 \quad + \text{ evaporation}$$

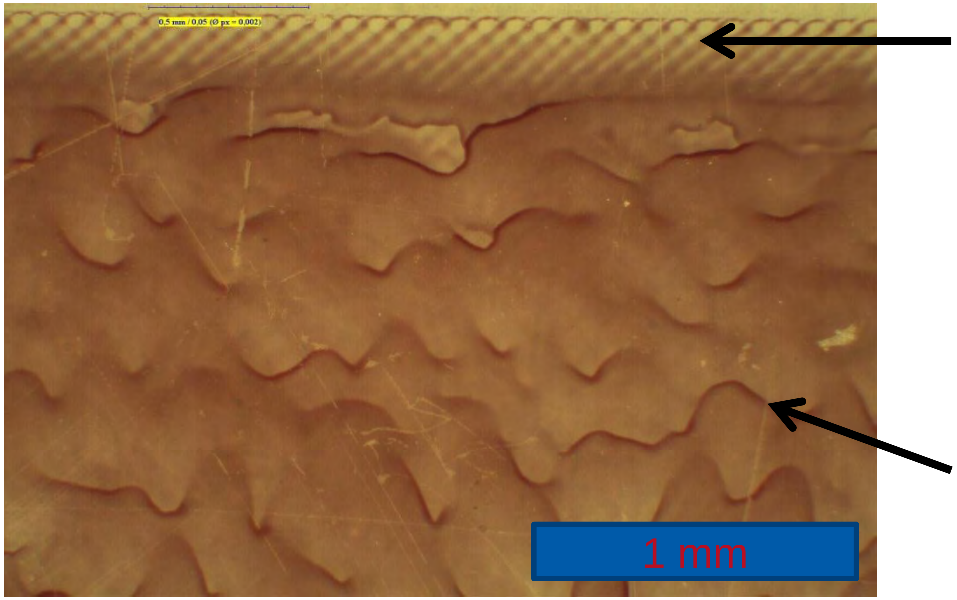


low solute concentration
-> high surface tension



high solute concentration
-> low surface tension

Marangoni vs. gravure raster related patterns in printed P3HT / toluene layers

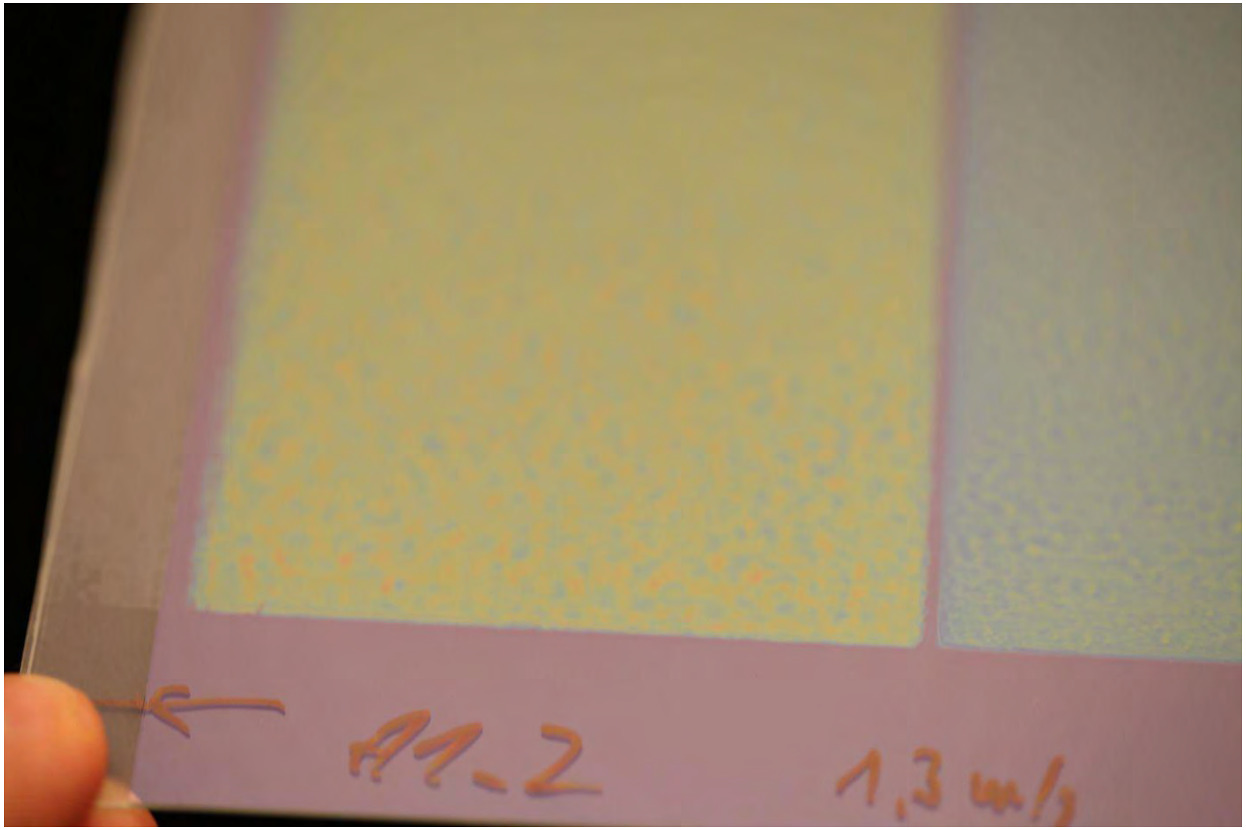


Patterns from gravure cells

Spontaneuous pattern formation from the solvent evaporation

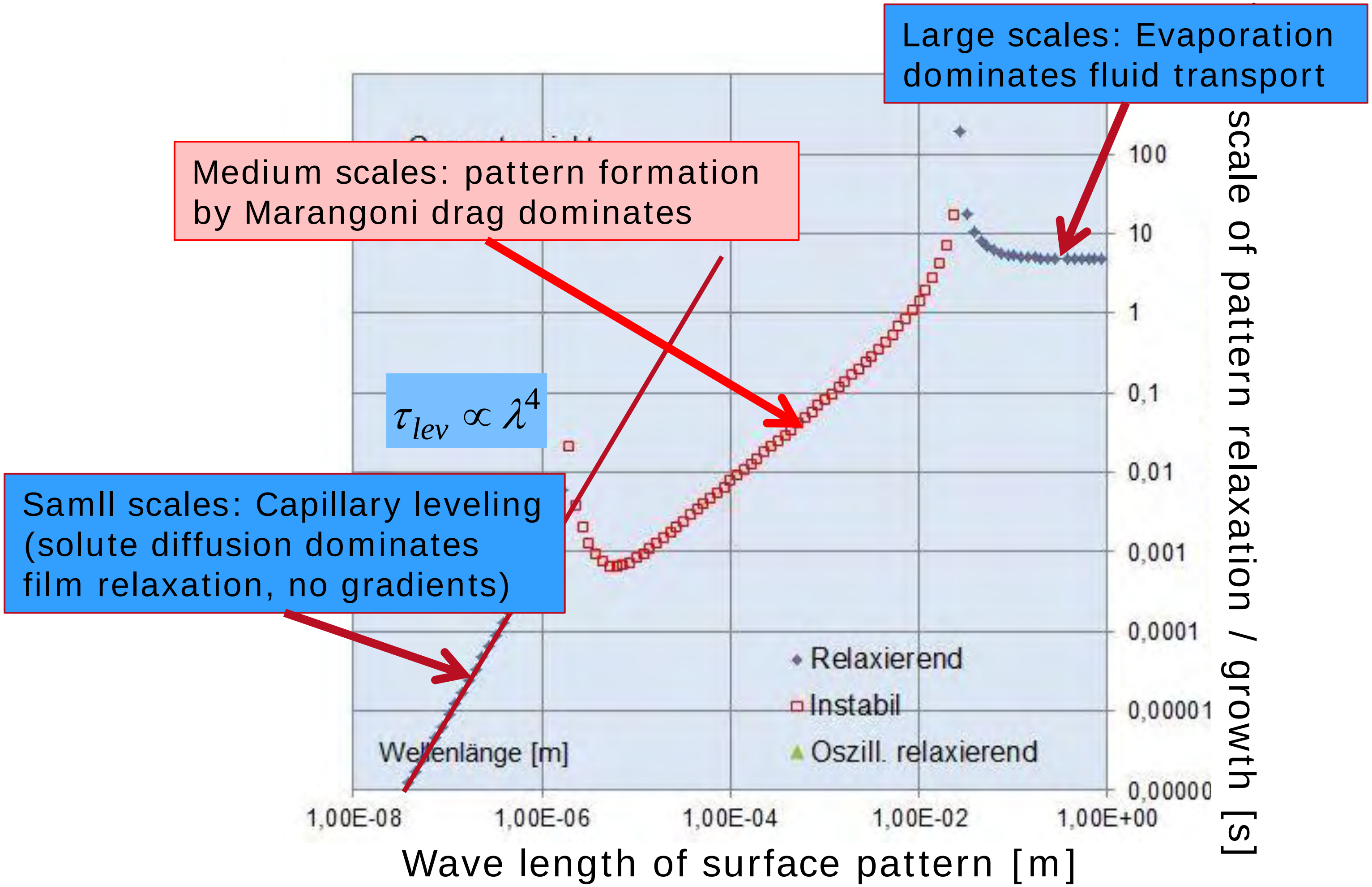
Gravure printed P3HT layer, from toluene solution (W. Bartonitz 2009)

Another example of pattern formation (~30 nm Spiro-MeoTAD/anisole)



How evaporation creates Marangoni flows

Pattern growth / relaxation rates on different scales (2K liquid film with evaporation)



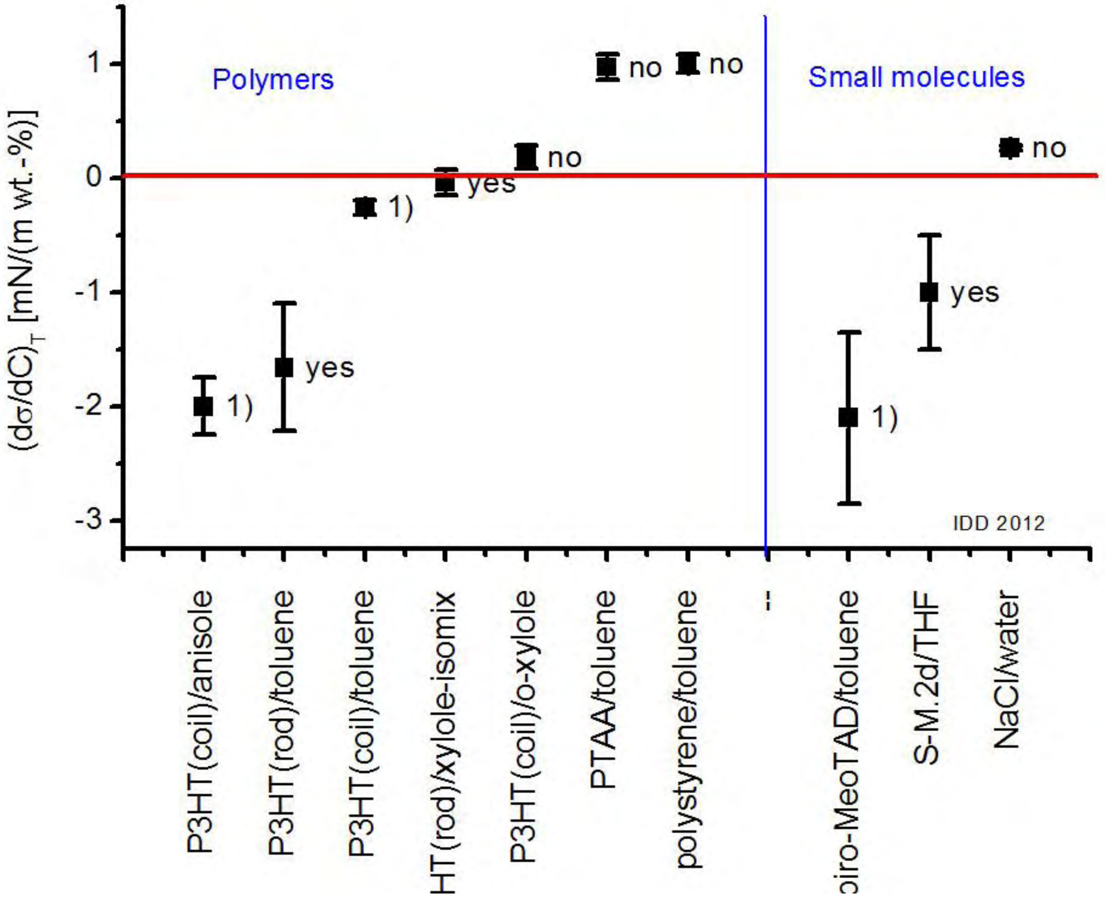
Large scales: Evaporation dominates fluid transport

Medium scales: pattern formation by Marangoni drag dominates

$\tau_{lev} \propto \lambda^4$

Samll scales: Capillary leveling (solute diffusion dominates film relaxation, no gradients)

$\delta\sigma/\delta C$-coefficients in diluted organic semiconductor solutions



Yes: drop flow observed

No: no drop flow

1): not clearly distinguishable

- Positive and negative $\delta\sigma/\delta C$ make a big difference for printing & drying
- Very small differences in surface tension (~0.1 mN/m) may induce pattern formation in thin liquid films.

Conclusion

- Printing (or making sth printable) has different aspects
- Printing is a sequence of physical subprocesses, accessible by hydro- & thermodynamical models
- The various printing techniques (inkjet, gravure, flexo,…) provide different, specific technical solutions to perform/control the individual subprocesses
- Printing (organic) semiconductor layers (OLED, OTFT, solar cells …) evokes phenomena, and requires a modification of printing techniques which are unknown in graphical arts
- Pattern formation in printed films (and avoiding it) is a thrilling competition with molecular, viscous, capillary, evaporation-related forces, which may prevail on different length scales.

Literature

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- Joel Emerson Neff, Master Thesis, 2009, Georgia Institute of Technology*, Investigation of the effects of process parameters on performance of gravure printed ITO on flexible substrates*
- Bornemann et. al., Evaluation and Determination of Gravure Cylinders for Functional Printing, Lope-C proceedings 2011
- H.M.Sauer, *Organische Halbleiter im Tief- und Flexodruck produziert*, Tief+Flexo-Druck 5/2013, p.18
- S. Manukyan et al, JCIS **395**, 287 (2013)
- H. M. Sauer, D. Daume, E. Dörsam, JPMTR **4**, 163 (2015)

Thank you for your attention

IDD youtube channel with more printing videos:
https://www.youtube.com/user/IDDvideokanal

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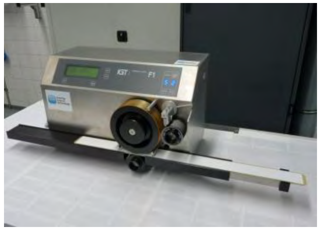
Step 1: Proof of Concept, Printability

Quantity of functional fluid: few milliliter

For fast tests with small quantities

- Offset Printability Tester IGT AIC2-5

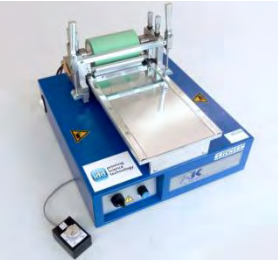
- Flexography and Gravure Printability Tester IGT F1



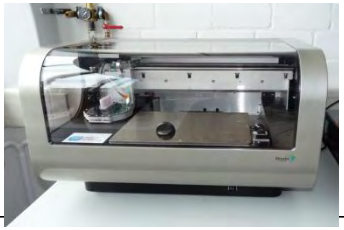
- Gravure Printability Tester IGT G1-5

- Gravure Printability Tester prüfbau

- Gravure and Flexo Printability Tester RK Printing Proofer



- DIMATIX Materials Printing System DMP-2831



Peripheral Equipment

Coating technology for reference layers

- Zehntner automatic film applicator
- SPS-Europe POLOS MCD200-NPP Spin-Coater

Equipment for substrate pre-treatment

- ASF Corona and Plasma System
- Diener Vacuum Plasma
  - Argon
  - Oxygen

Peripheral Equipment
Heating, Post-Treatment

Coating technology for reference layers

- UV-, IR- and Heat-Dryer
- Hotplates
- Oven, oven with vents for solvents

Equipment for photonic sintering

- NovaCentrix PulsForge 1200

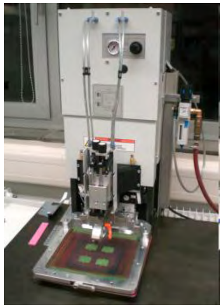
Step 2: Rapid Prototyping, Lab printing DIN A4

Quantity of functional fluid: min. 100 ml

“Lab-size” functional and graphic printing

- Flexo Labor Printer FLP-21
- Flexo Printing Machine F500
- KAMMANN (Screen Printer)
- Saueressig Gravure Lab Printing Machine
- HEIDELBERG QUICKMASTER 46-2 (Offset Printing)
- Hot-Stamping Machine Baier Geba 6






Step 3: Mass Production, Inline processing

Quantity of functional fluid: min. 1 l

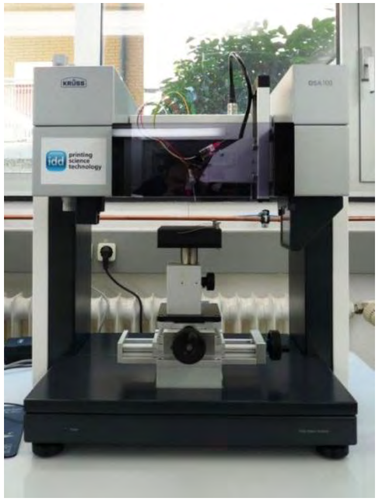
Roll-to-Roll printing with all conventional (flexo, offset, gravure, screen) printing technologies and an Inkjet unit

Modular web-fed press – GALLUS RCS 330-HD

Climate Laboratory usable for Step 1 and 2, Material characterization

Climate Laboratory

Printing tests at standard climate (23°C, 50% RH)



Contact Angle Measuring KRÜSS DSA 100

Bubble Pressure Tensiometer KRÜSS BP100

Particle Sizing System Nicomp 380 DLS

Materials testing Machine ZWICK Z050 – Characterization of the viscoelastic properties of substrates (foil, paper), blankets, flexographic printing plates, ...

Rheology Lab

Characterization of fluids (viscoelasticity, extensional viscosity)

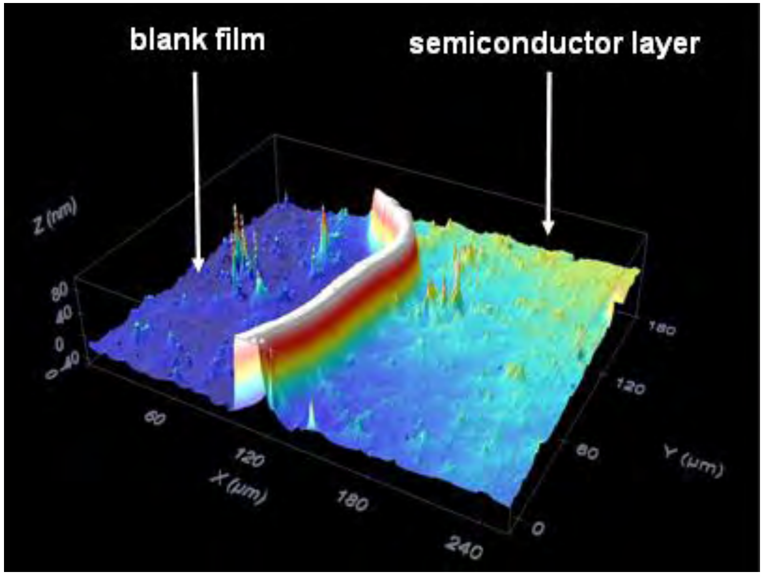
- Haake MARS III Rheometer (rotation, oscillation)
  - Equipped with UV-Curing Cell and High-Shear Option
- Haake CaBER Extensional Rheometer
  - Equipped with normal force and positioning sensors

Optical Characterization

Sensofar Plµ Neox

Leica DM4000M

Example: P3HT layer 20 – 30 nm



Source: IDD - TU Darmstadt