Influence of surface nanostructure on wetting properties

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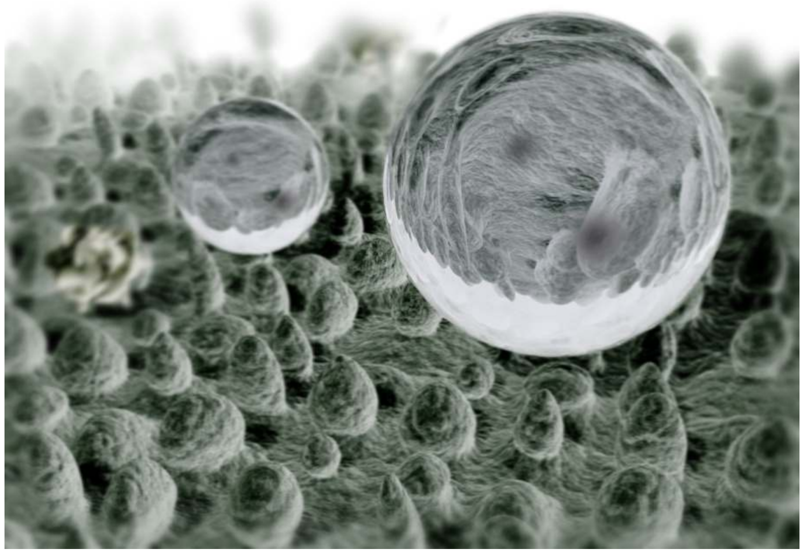
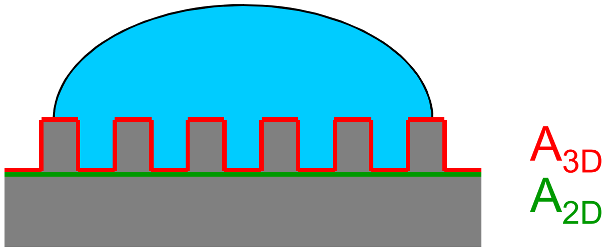
Introduction

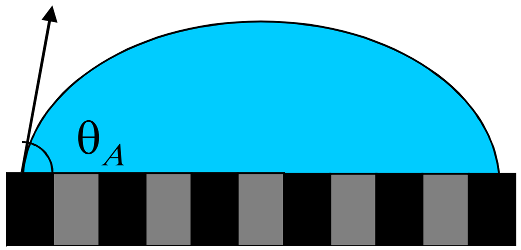
- Wettability is an important phenomenon in many industrial processes, e.g. adhesion, printing, self-cleaning surfaces etc.
- The wettability of a surface is governed by the chemistry and the morphology of the surface.
- A classical example is the self-cleaning properties of the lotus leaf (ref. Barthloot, W., Neinhuis, C. *Planta* **1997**, 202, 1-8)



How to model wetting of nanopatterned surfaces?
How can we utilize wetting for optimized printing aquality?

Wetting of rough and heterogeneous surfaces





$$\cos\theta_A = r\cos\theta_Y$$

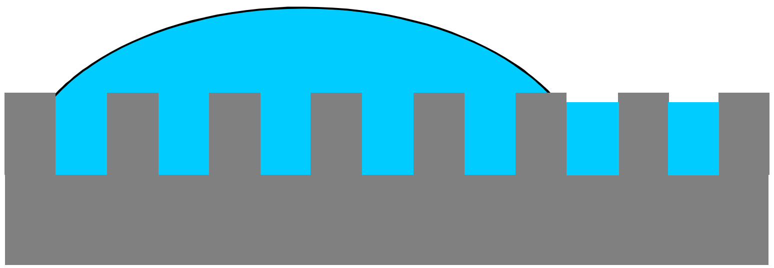
$r = A_{3D}/A_{2D}$

Wenzel

$$\cos\theta_A = f_1\cos\theta_1 + f_2\cos\theta_2$$

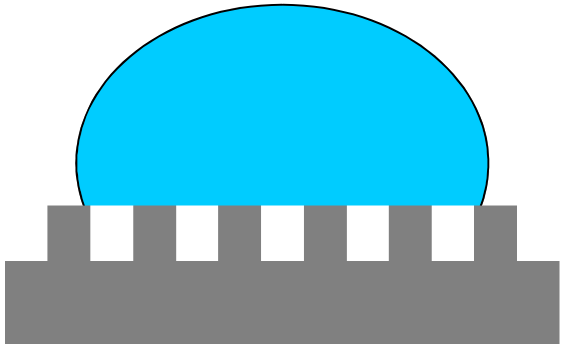
Cassie

Wetting of rough and multicomponent surfaces



$$\cos\theta_A = f_S \cos\theta_S + (1 - f_S)$$

Bico



$$\cos\theta_A = f_S \cos\theta_S - (1 - f_S)$$

Cassie-Baxter

Contact angle hysteresis!

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Evaluation of wetting therories for nanometer-length scale heterogeneities

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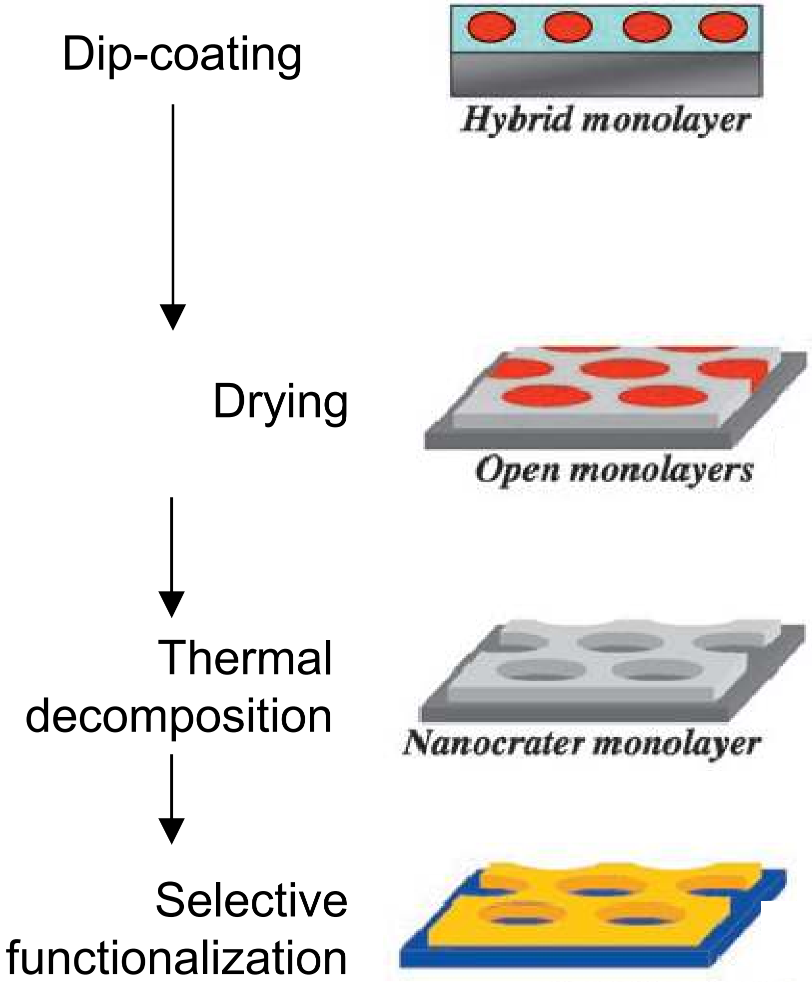
Synthesis of model substrates



The pore diameter can be tuned between 10 and 50 nm depending on the size of the block-copolymer used as the template.

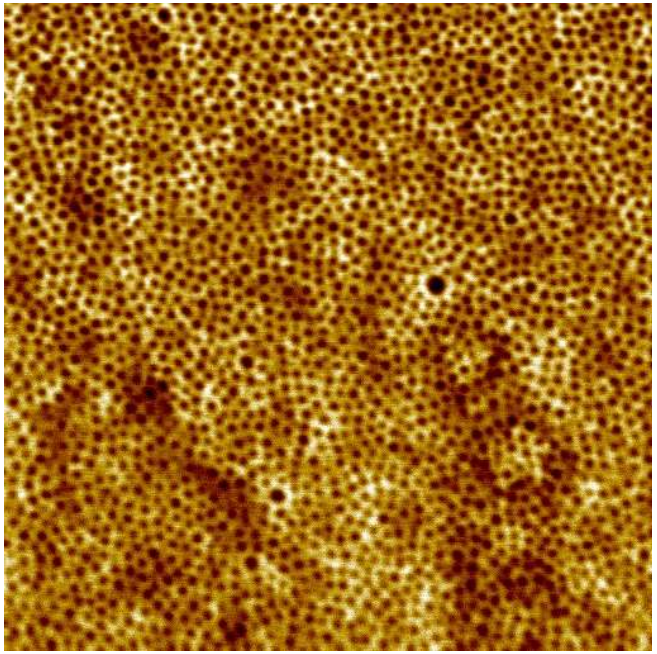
Pores are aligned perpendicular to the substrate, which make these films ideal for applications related to microelectronics and sensing, to name a few.

The substrate (SiO_2 or Au) is accessible through the craters.

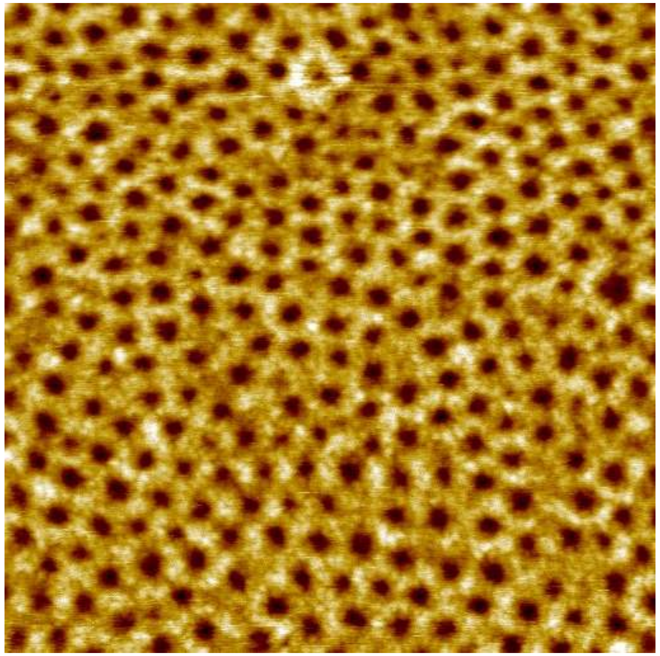
A. Fisher, M. Kuemmel, M. Järn, M. Linden, C. Boissière, L. Nicole, C. Sanchez, D. Grosso, *Small* **2006,** *2*, 569.

Nanopatterned $TiO_2@SiO_2$

3 µm × 3 µm



1 µm × 1 µm

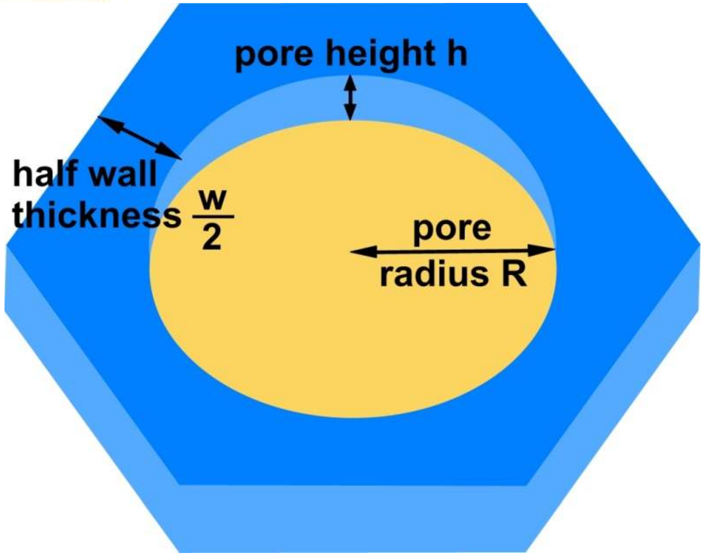


Pore diameter ≈ 30 nm

Wall thickness ≈ 30 nm

Layer thickness ≈ 2 nm

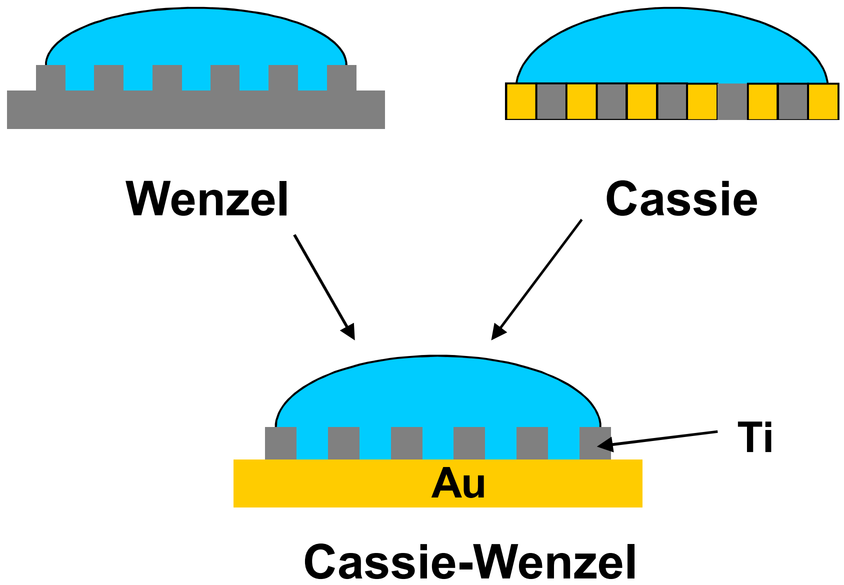
Determination of critical parameters



f and *r* values are determined from one unit cell (AFM, SEM, ellipsometry)

$$f_{TiO2-2D} = 1 - \frac{\pi R^2}{2\sqrt{3}\left(R + \frac{w}{2}\right)^2}$$

$$r = 1 + \frac{2\pi Rh}{2\sqrt{3}\left(R + \frac{w}{2}\right)^2 - \pi R^2}$$

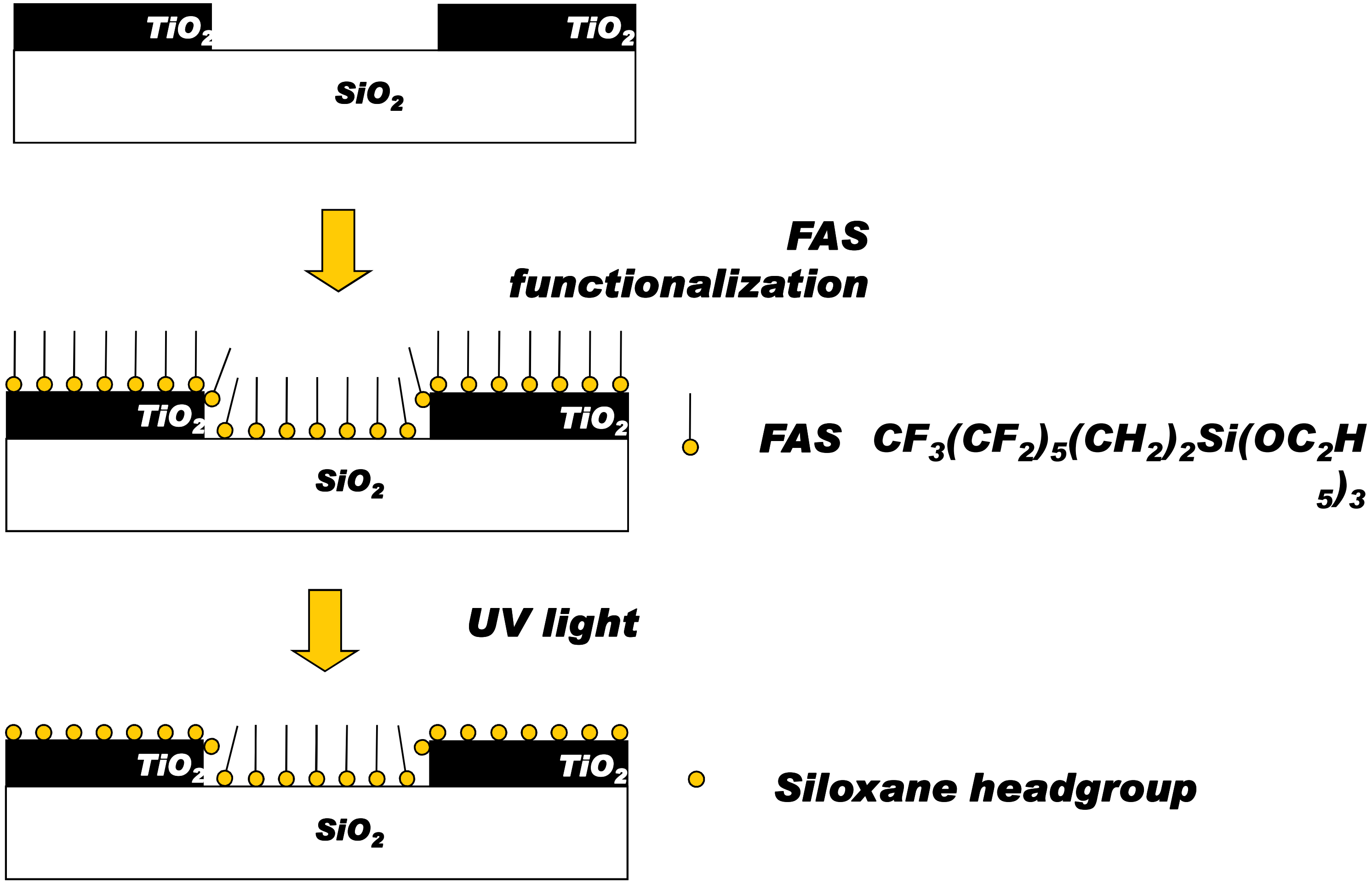


$$\cos\theta_A = F_{Ti}\cos\theta_{Ti} + F_{Au}\cos\theta_{Au}$$

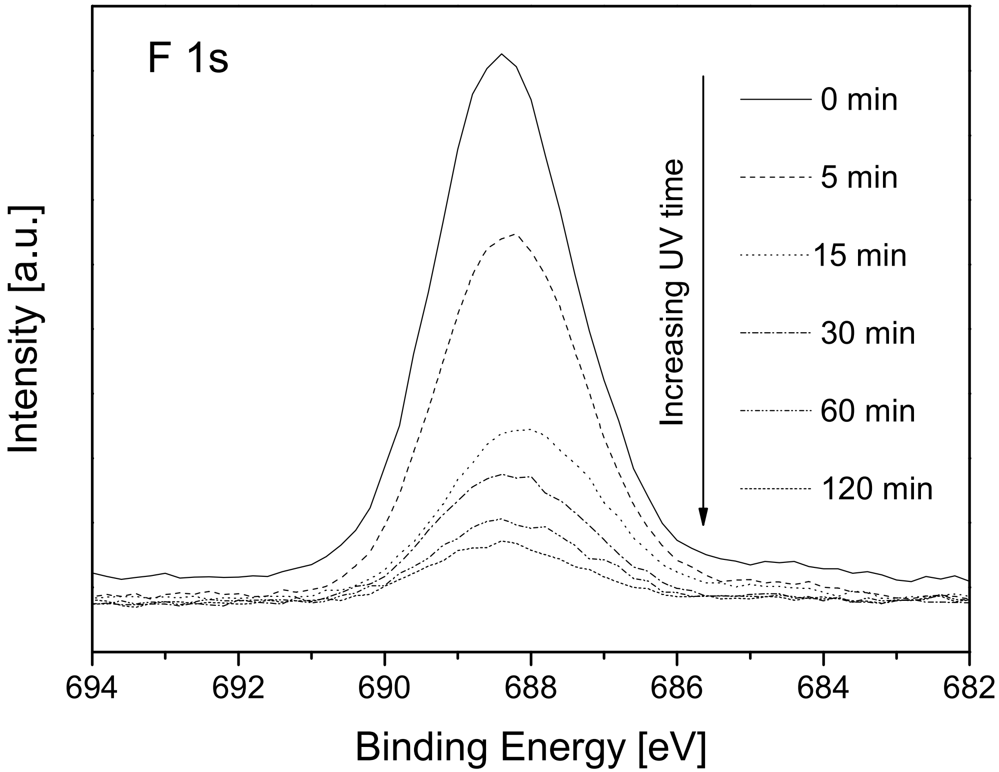
$$F_{Ti} = \frac{r \cdot f_{Ti}}{r \cdot f_{Ti} + f_{Au}} \qquad F_{Au} = \frac{f_{Au}}{r \cdot f_{Ti} + f_{Au}}$$

M. Järn et al. *Chem. Mater.* **2008**, *20*, 1476.

Variation of f-values

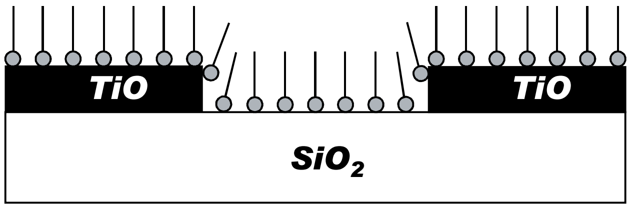


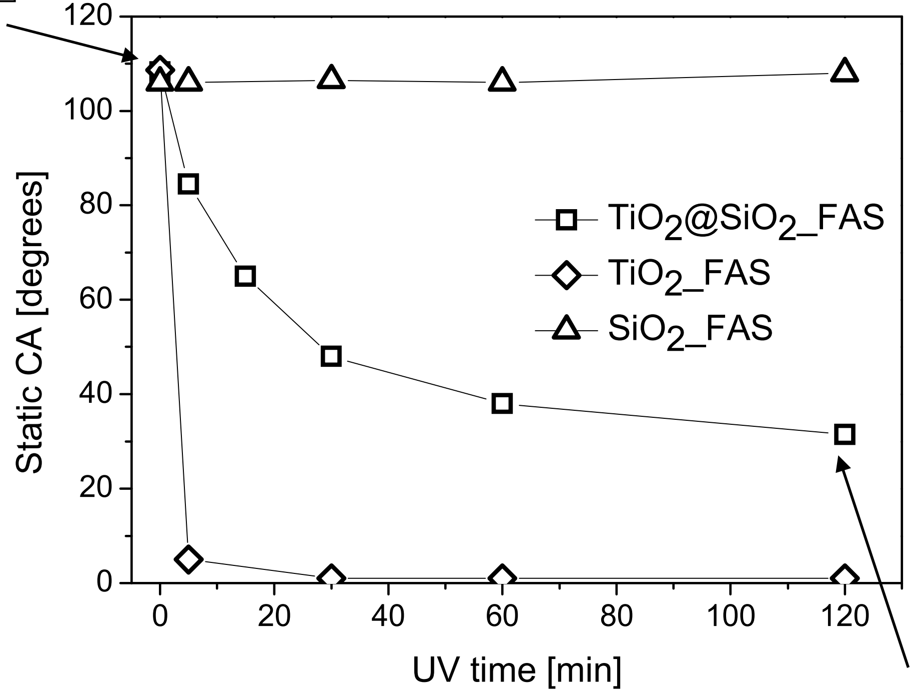
Verification of f-values



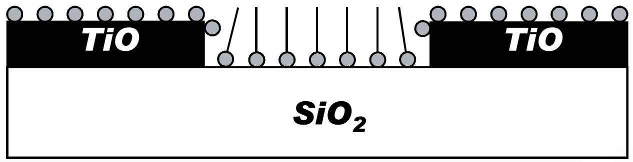
UV time [min]	**0**	**5**	**15**	**30**	**60**	**120**
F/Ti	2.34	2.03	0.91	0.72	0.42	0.32
f_{FAS}	1	0.87	0.39	0.31	0.18	0.14

Contact angle results





M. Järn, Q. Xu, M. Lindén, *Langmuir, In Press*



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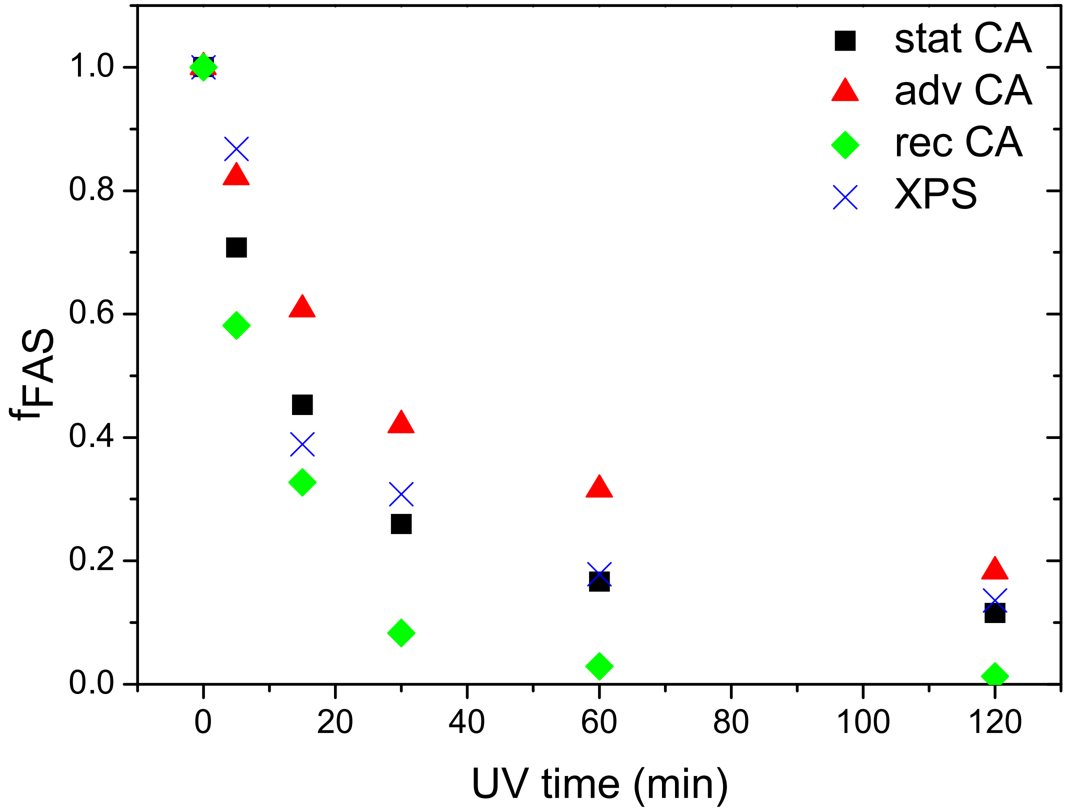
Static contact angle gives the best agreement!



f_{FAS} values calculated from the static CA give a good agreement with the XPS data

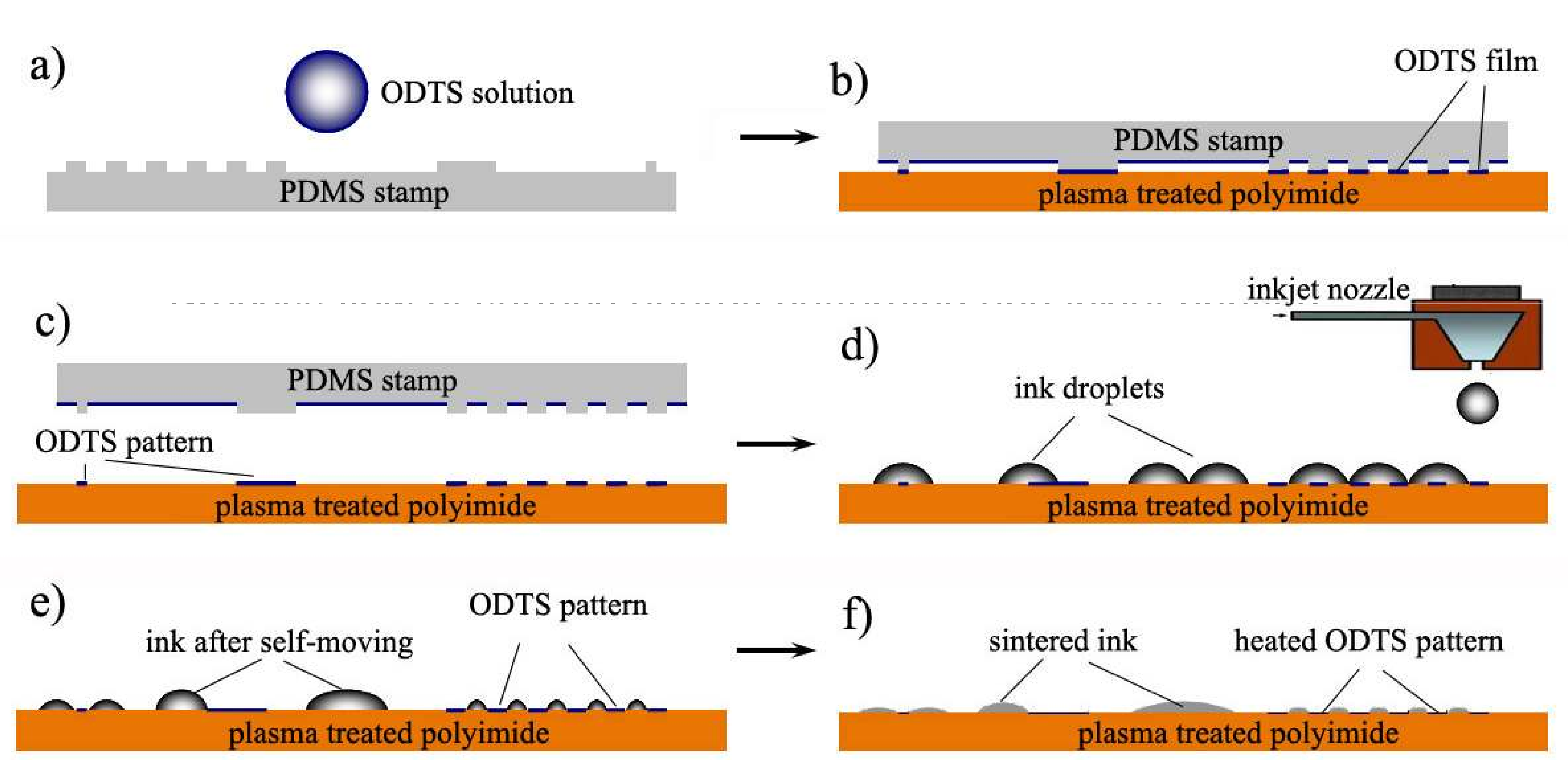
Applied wetting studies

Goal: higher resolution in inkjet printing

- Normally resolution is 35-100 μm, 20 μm is the limitation for most inkjet printing.
- OFET channels require controlled geometries below 20 μm
  - Shorter channels lead to higher performance,
  - Less material consumption
- One of the most challenging issues for inkjet printing technology.

Our method: stamping

Stamping: *a fast and easy way to replicate patterns generated by photolithography (≥1μm), electron beam lithography (nm), or other methods.*

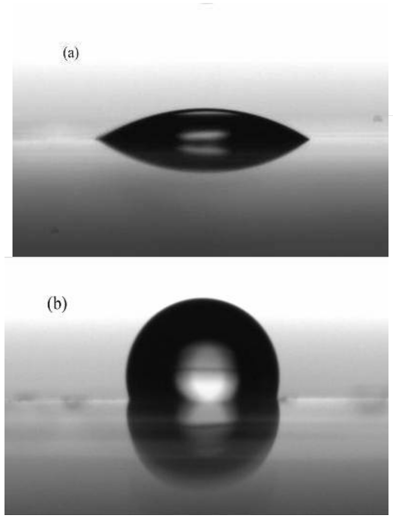


J. Lin, M. Lindén R. Österbacka et al., Submitted

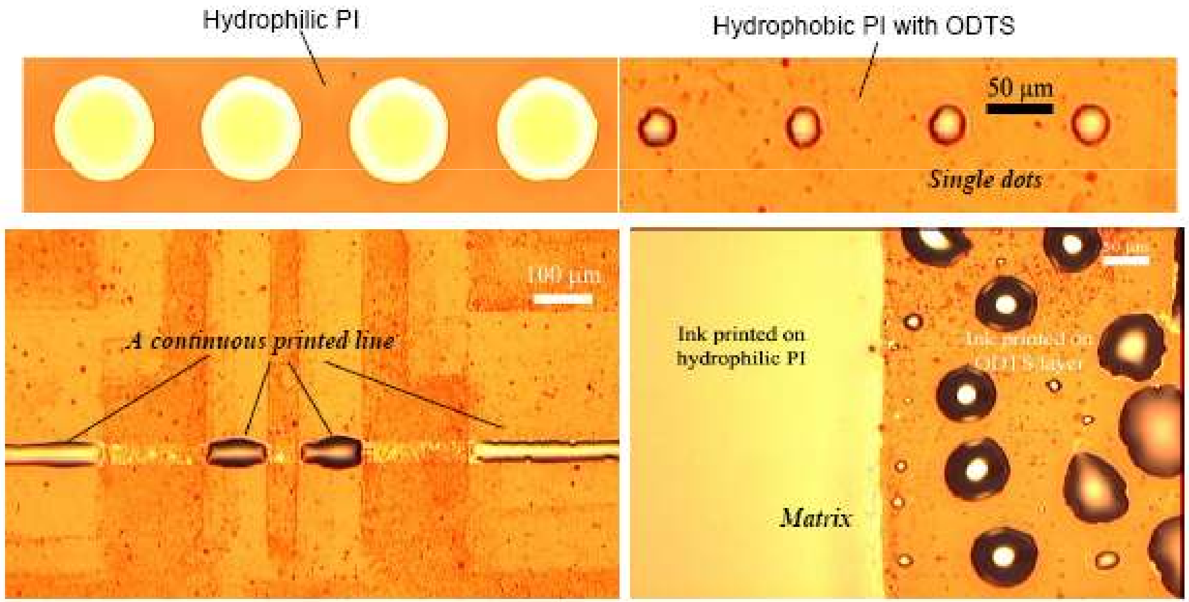
Inkjet printing results

Surface energy patterning controls print quality in printed electronics

- For better control of quality
- For increased resolution



Water contact angle



Comparison of ink printed (dots, line, and plane) between areas with ODTS layer and without ODTS layer

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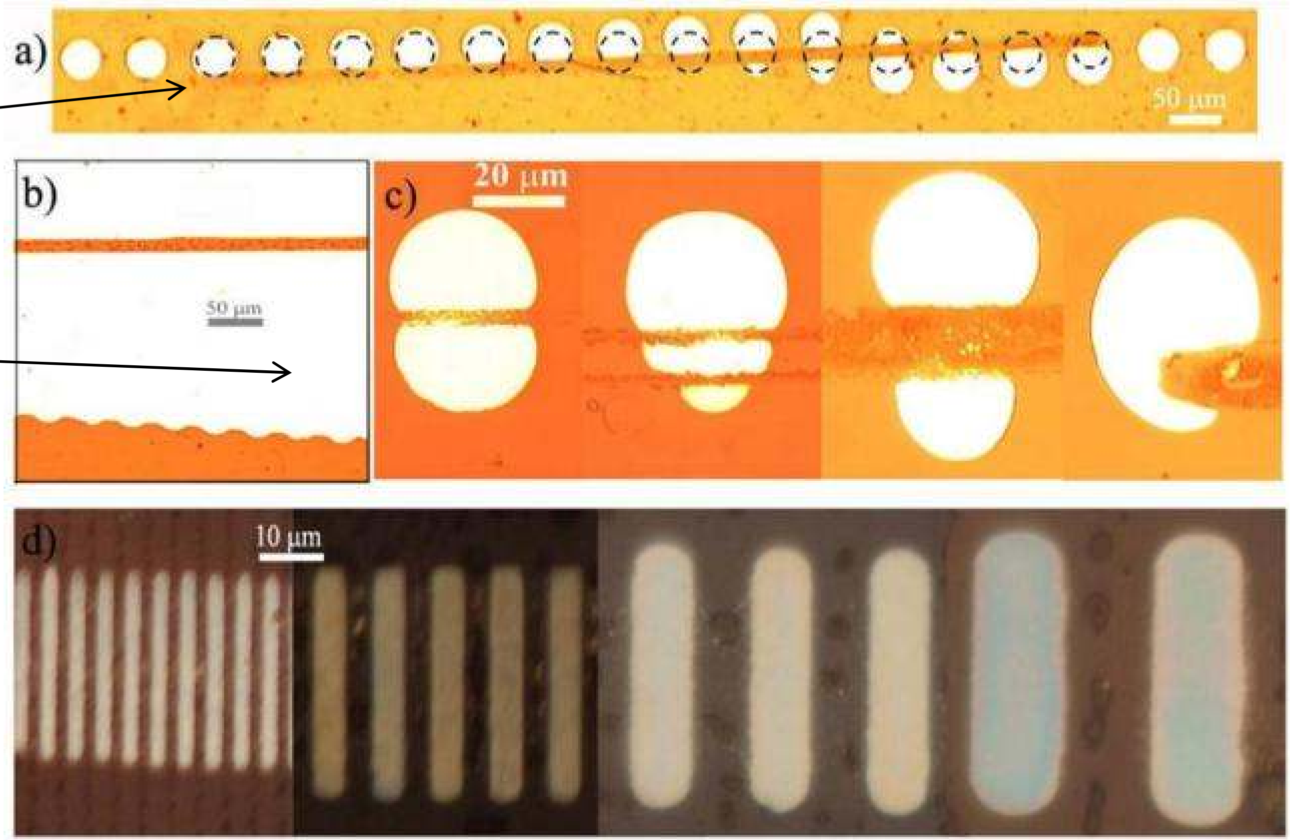
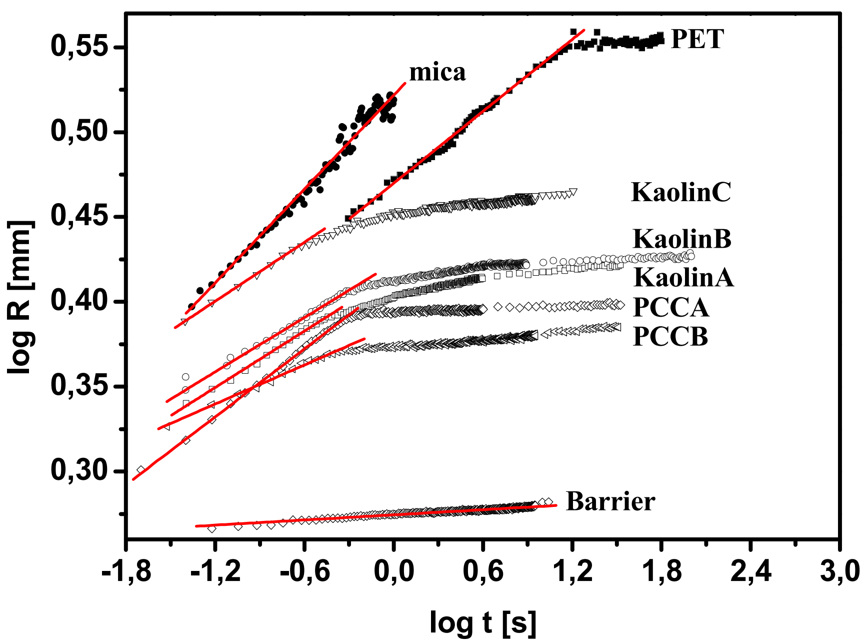
Inkjet printing results

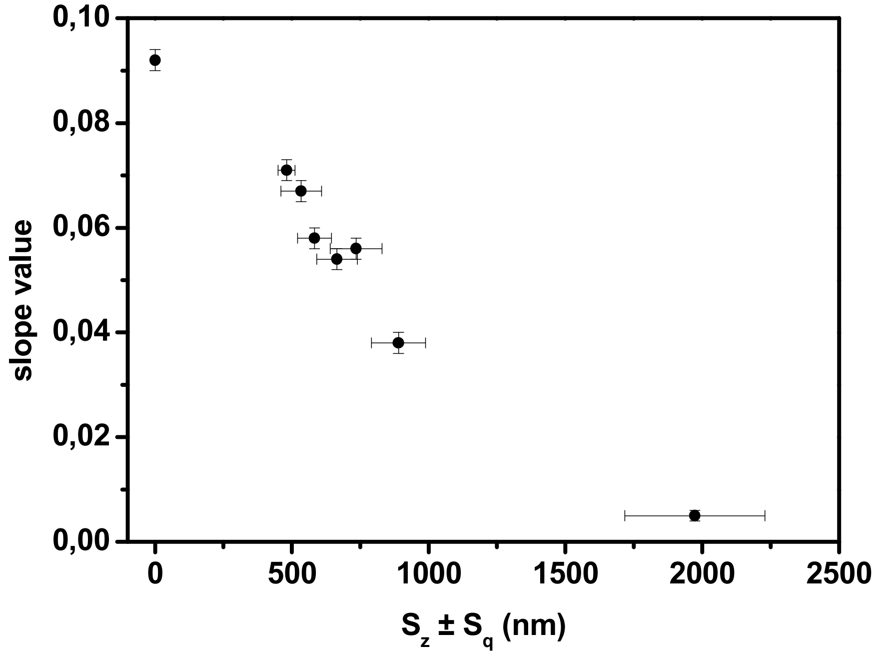
- Surface pattern controls print quality
- Patterning gives better control over printed edges compared to non-patterned
- Better resolution!
- **Resolution limited by stamp fabrication!**
- Good for making short channel devices



2 µm 4 µm 8 µm 12 µm

Wetting kinetics of o-DCB* on coated paper





- Maximal spreading of inkjet droplets (radius R) of o-DCB* is dependent on roughness, surface energy, pore volume and geometry of the paper coating.

- The wetting rate (slope) correlates with the magnitude of surface extremes (asperities, S_z).

*ortho-dichlorobenzene , a typical solvent for semiconductor P3HT

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A. Määttänen, P. Ihalainen, M. Toivakka, R. Bollström, J. Peltonen: **Colloids Surfaces A, submitted.**

Conclusions

- Detailed wetting studies on well-characterized nanopatterned surfaces suggest that the static contact angle is the most reliable measure of surface heterogeneities when on the nanometer length scale
- Rational substrate optimizations for printing can be performed for enhanced print-resolution for preparation of advanced strucures
- Surface structure, polarity, and porosity do all have to be taken into account for optimized spreading. However, surface topography has an almost linear influence on the wetting rate.