

Ultrathin films

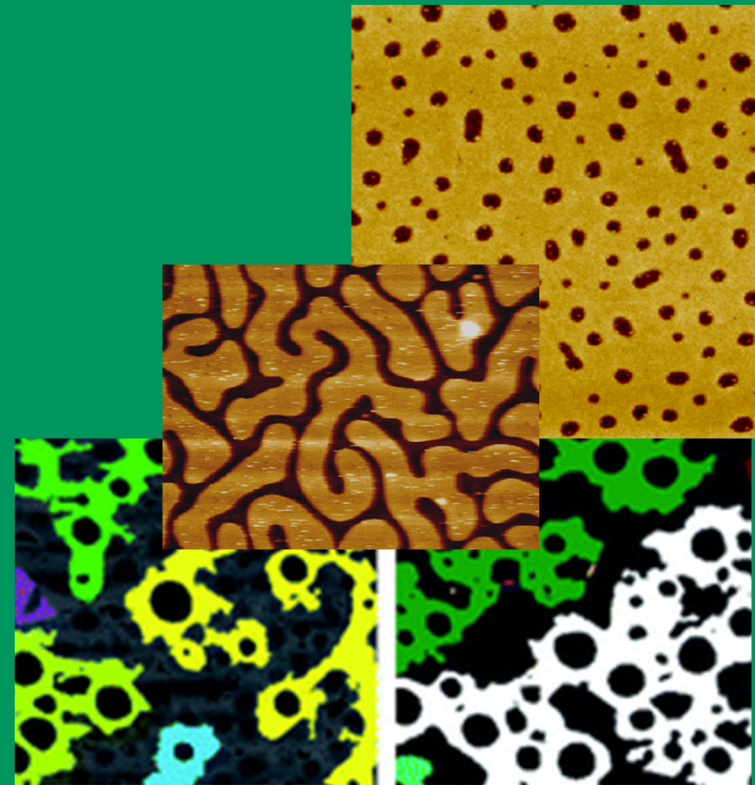
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CHEM-L2000

Eero Kontturi

3rd March 2022



Aalto University
School of Chemical
Engineering



Learning objectives

- To be aware of what an ultrathin film is
- To understand why surface analysis is important
- To be aware of the distinction of a model surface
- To have knowledge of the common preparation techniques and analytical methods for ultrathin films
- To be able to choose a proper analytical technique for an ultrathin film for a designated purpose

NOTE: All topics in the course are geared towards *soft materials*

Lecture schedule

Time / Date	Thu 3rd March	Fri 4th March	Mon 7th March	Fri 11th March		
9-10		Atomic Force Microscopy II: Colloidal Probe Monika Österberg				
10-11	Ultrathin films: Introduction Eero Kontturi		Electron Microscopy Eero Kontturi	X-ray Photoelectron Spectroscopy Kristoffer Meinander		
11-12						
12-13						
13-14	Quartz Crystal Microbalance Tekla Tammelin				Basic methods for film deposition: Langmuir-Blodgett and spin coating Eero Kontturi	Ellipsometry/ X-ray Reflectivity Eero Kontturi
14-15						
15-16	Atomic Force Microscopy I: Fundamentals Eero Kontturi		Surface Plasmon Resonance Spectroscopy Eero Kontturi	Atomic Force Microscopy III: Special tools Eero Kontturi		
16-17						

Literature review

- Main task in the course
- The lectures are designed to help you with writing the review
- Involves ca. 15 articles, chosen by the course lecturers
- Organization of the text is up to the participant but the text should be lucid and fluent
- The review must be written in proper English without a constant flow of mistakes
- Critical approach
 - ✓ Which analytical methods would have brought added value to the work?
 - ✓ Could the interpretation be stronger?
 - ✓ Any false assumptions? (...and so on)

Literature review

- Grading depends largely on the degree of criticism that you are able to include in the review
- Coherence: try to find a common denominator in all the articles (at least they are all about ultrathin films in one way or another)
- Propose an experiment or a small set of experiments, inspired by the articles in the review, that fits in with your own research
- Besides the written review, each student gives a short seminar presentation (~15 min) during the seminar day

The seminar is scheduled for May/June 2022

Deadline for submitting the review is Friday 20th May 2022

Outline – introductory lecture

- (1) Surface analysis – why?
- (2) Surface analysis on bulk objects
- (3) Ultrathin films
 - model surfaces
 - material aspects
- (4) Preparation of ultrathin films
- (5) Characterization of ultrathin films
- (6) Research example: ultrathin film of cellulose
- (7) Summary

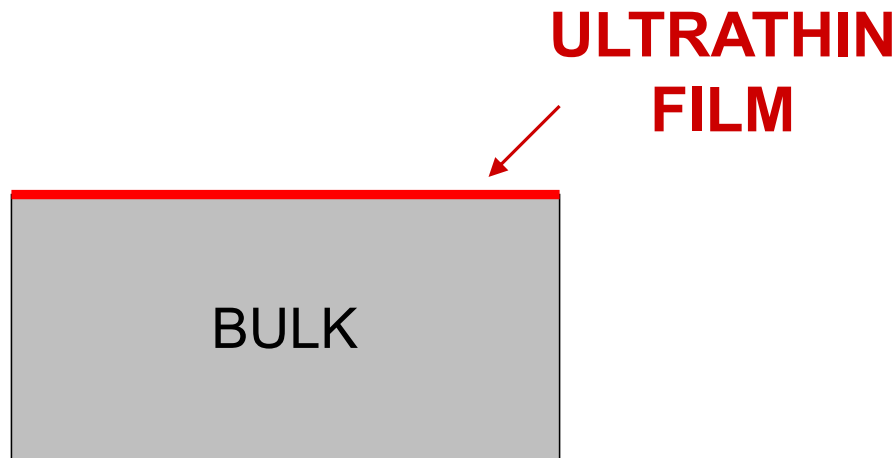
Surface analysis – why?

Surface *practically always* bears properties that are different from bulk.

- Surfaces are important: they are material's contact to the outside world
- Many material properties are directly dictated by the surface:
 - adhesion (bonding with other substances)
 - hydrophilic/hydrophobic character (mostly)
 - many optical properties
 - roughness (friction)
 - etc.

Surface analysis – why?

Sometimes a surface is made intentionally for a variety of purposes



Surface analysis – why?

The bottom line is: *surface analysis is always challenging.*

- Bulk methods almost never work for surface characterization
 - Material-wise, the amount of surface is always small compared with the bulk (although the surface area may sometimes be great)
- There are analytical methods designed solely for surface analysis
- Surface analysis is a vast area of scientific research

Surface analysis of bulk objects

Surface analysis in general has two aspects:

- (1) Chemical composition and physical properties of the surface
- (2) Physical appearance of the surface (morphology)

Surface analysis of bulk objects

Methods to determine the chemical composition of the surface:

X-ray photoelectron spectroscopy (XPS)

Secondary Ion Mass Spectrometry (SIMS)

Surface sensitive variants of Raman and IR spectroscopy

Methods to determine surface morphology:

Atomic Force Microscopy (AFM)

Scanning Electron Microscopy (SEM)

Problem: most other surface-sensitive methods do not work for bulky objects but only for ultrathin films.

→ Solution: prepare ultrathin models of bulky substances, i.e., model surfaces or model films

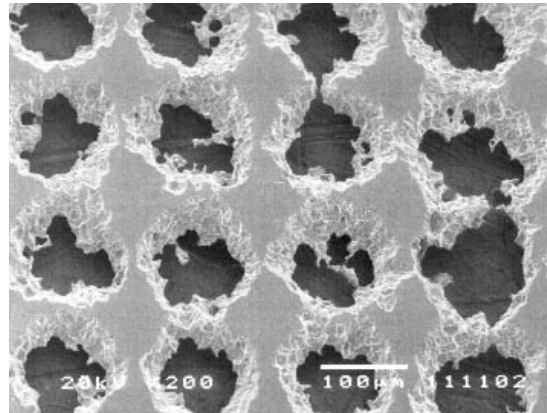
Definition: ultrathin film

Thick films



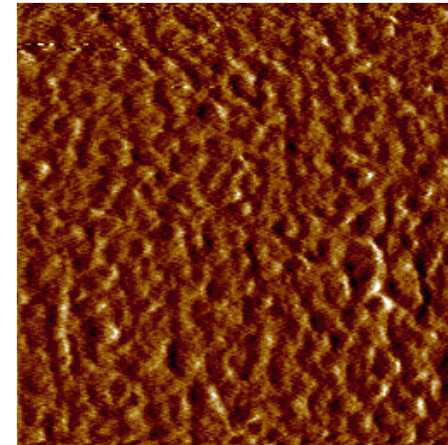
$> 1 \mu\text{m}$

Thin films



100-1000 nm

Ultrathin films



$< 100 \text{ nm}$

Analysis of ultrathin films

Methods to determine the chemical composition of the surface:

X-ray photoelectron spectroscopy (XPS)

Secondary Ion Mass Spectrometry (SIMS)

Surface sensitive variants of Raman and IR spectroscopy

Mössbauer Spectroscopy

Electron Energy Loss Spectroscopy (EELS)

Methods to determine the physical properties of a surface:

Ellipsometry

X-ray reflectivity (XRR)

Quartz Crystal Microbalance (QCM)

Surface Plasmon Resonance (SPR)

Methods to determine surface morphology:

Atomic Force Microscopy (AFM)

Scanning Electron Microscopy (SEM)

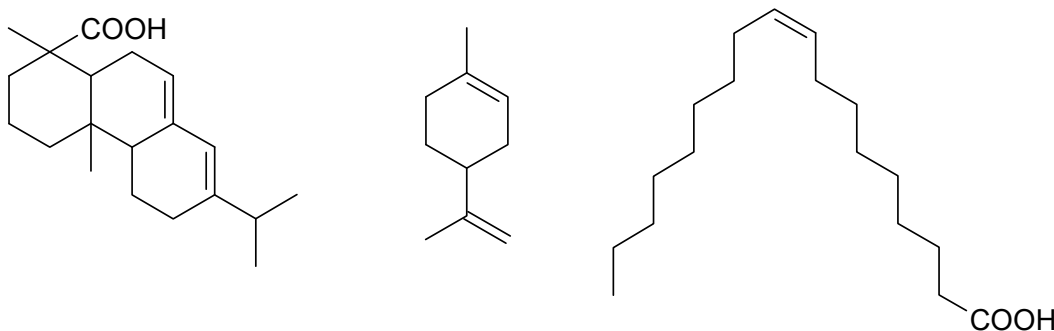
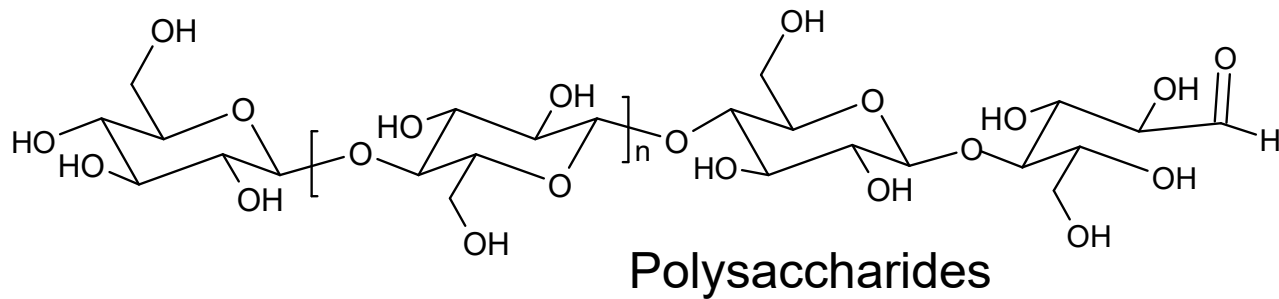
Scanning Tunneling Microscopy (STM)

Use of ultrathin model films clearly extends the palette of analytical methods.

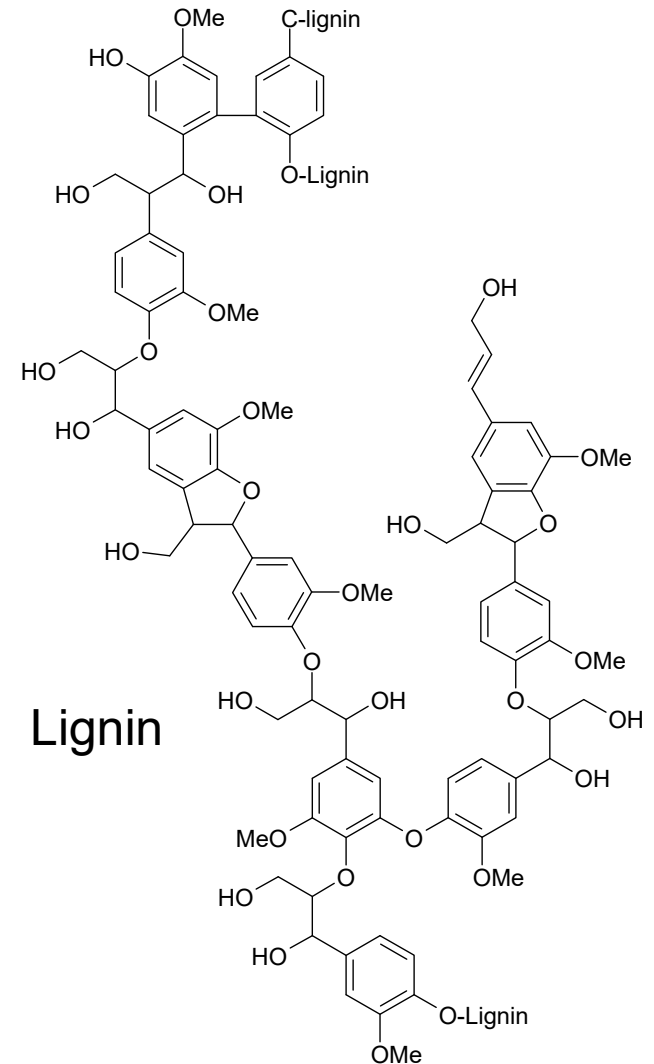
Further reasoning for model films

Example: wood fibres

Chemically heterogeneous

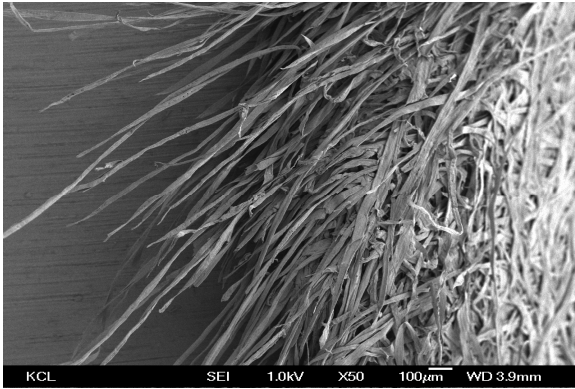


Small M_w organic compounds
(extractives)

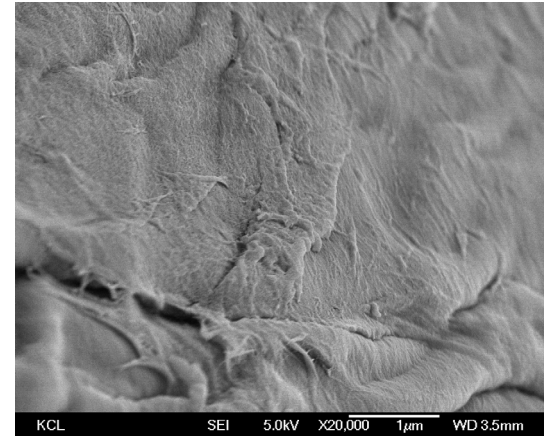
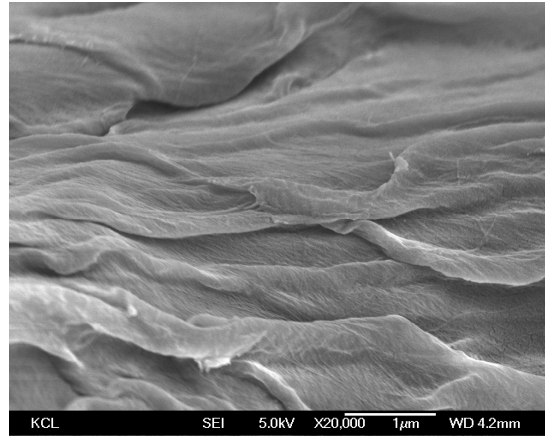
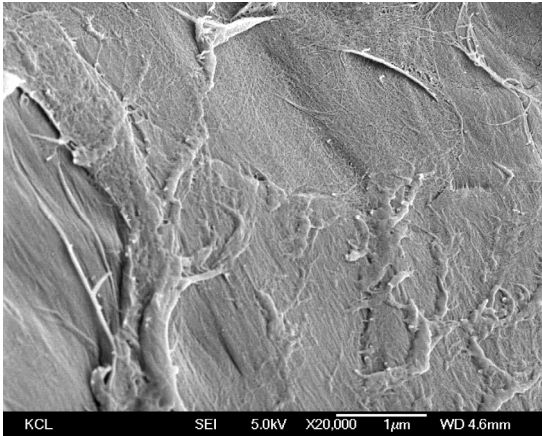


Further reasoning for model films

Example: wood fibres



- a lot of fibres in wood
- **morphologically heterogeneous**
(every single fibre is an individual)

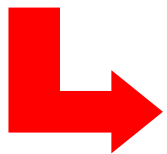


What is a model surface?

Model surface has two prerequisites:

- (1) Defined chemical composition (as with model *compounds*)
- (2) Defined morphology

NOTE: Model surface does not have to be an ultrathin film. Colloidal spheres, for instance, have a well defined chemistry and morphology and they can be utilised as model surfaces.



Hence, ***model film*** is an often applied term for an ultrathin film which is used as a model surface.

Reasoning for ultrathin films

Model films are just one aspect of ultrathin film usage.

There are broadly speaking two areas of utilization in scientific research:

(1) Model surfaces

- films are used as tools for fundamental research

(2) Templates for materials science

- ultrathin films possess properties that thick films or bulk materials lack

Ultrathin films as materials

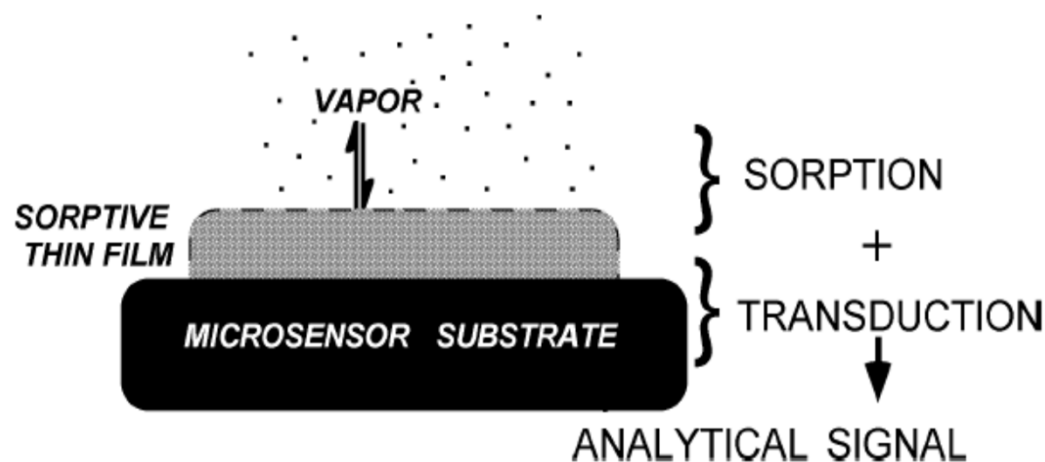
Functional materials

- **Sensors**
 - **Transistors**
 - **Photonic devices**
 - **Receptors**
 - **Templates for nanomaterials**
- etc.**

Usage of ultrathin films as functional materials is a huge area of research

Example: ultrathin film materials

Humidity/vapour sensor

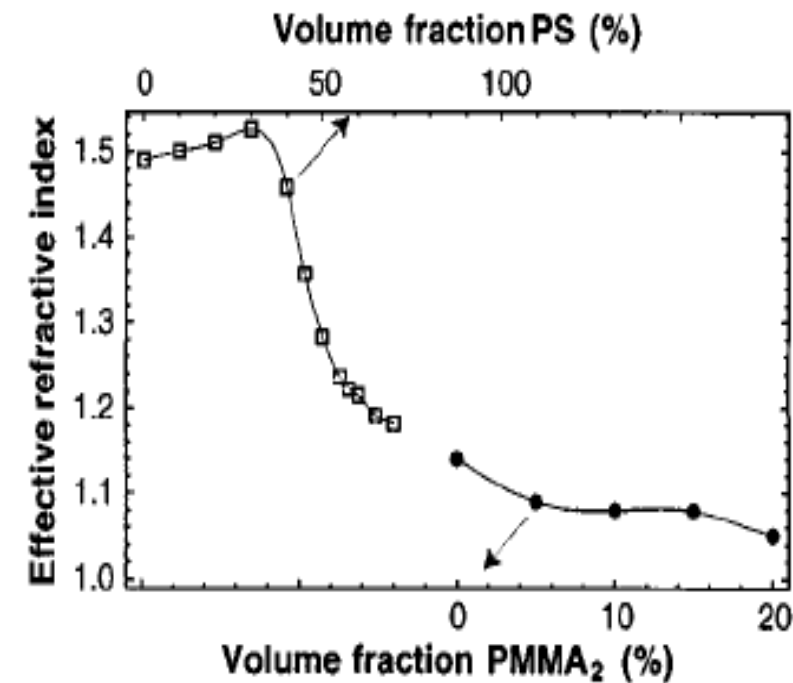


Hygroscopic polymer film promotes the sorption of vapours on the device surface.

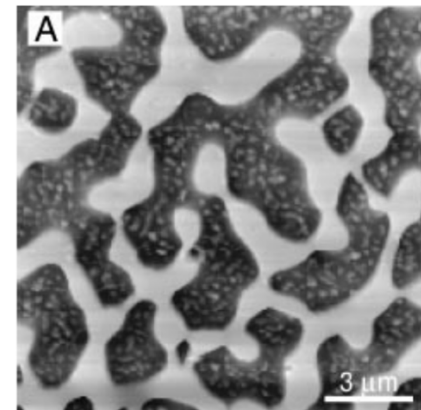
➡ **Sensor response is increased.**

Example: ultrathin film materials

Antireflective coatings from polymer blend thin films



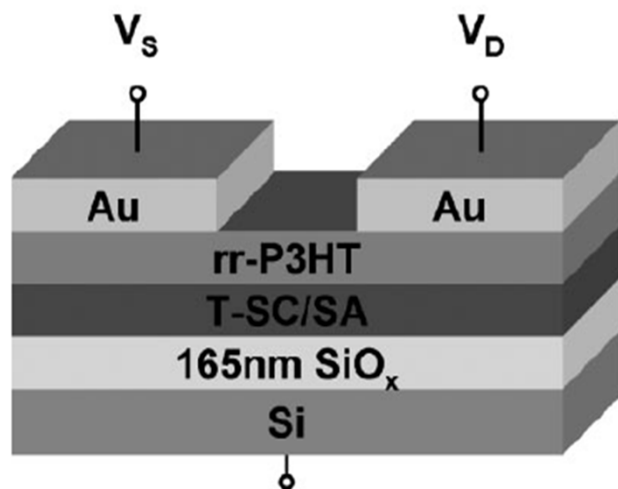
Polymer blend (PS/PMMA) is coated on a support
→ The other component is selectively dissolved
→ Nanoporous polymer film results
→ Antireflective properties at certain pore sizes
(when near the wavelength of light)



Example: material

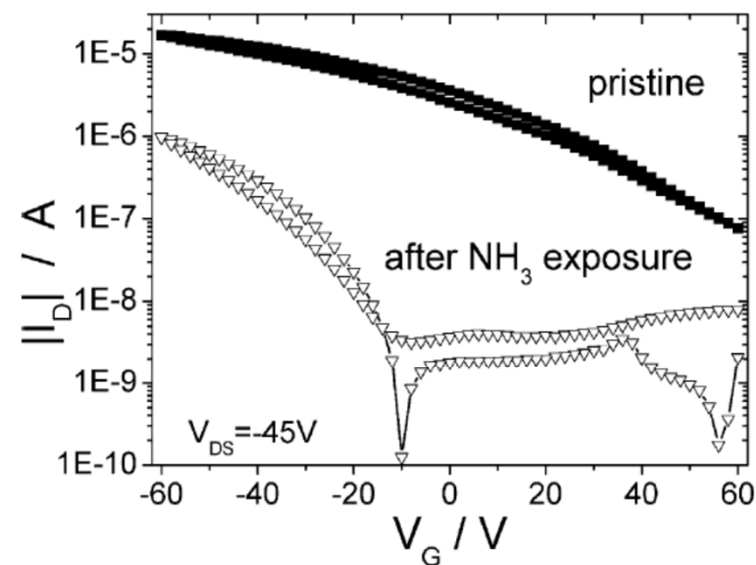
ULTRATHIN FILM AS AMMONIA GAS SENSOR

Cross sectional setup
of organic thin film transistor:

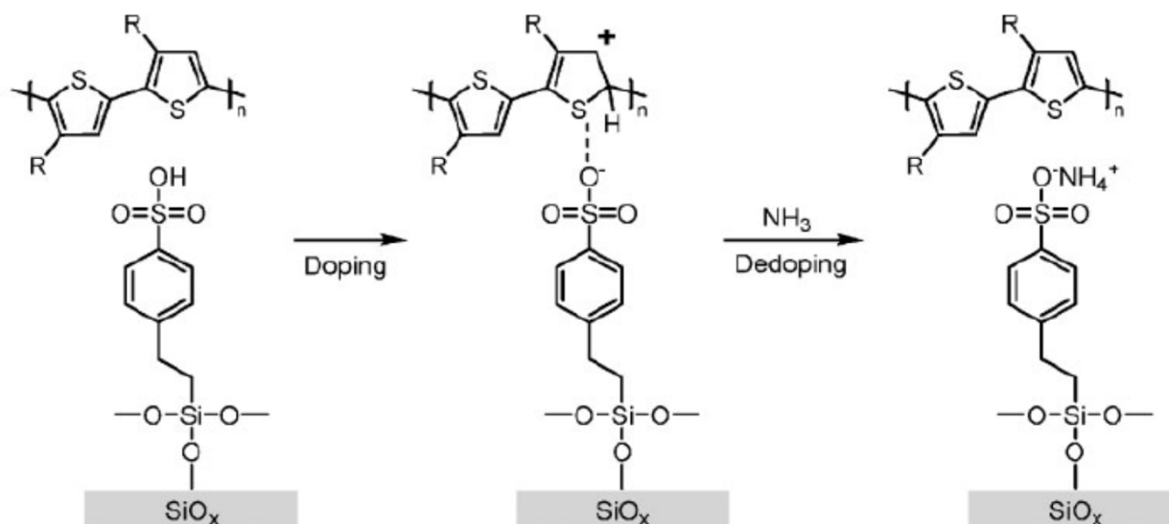


Detection
mechanism

Detection of ammonia

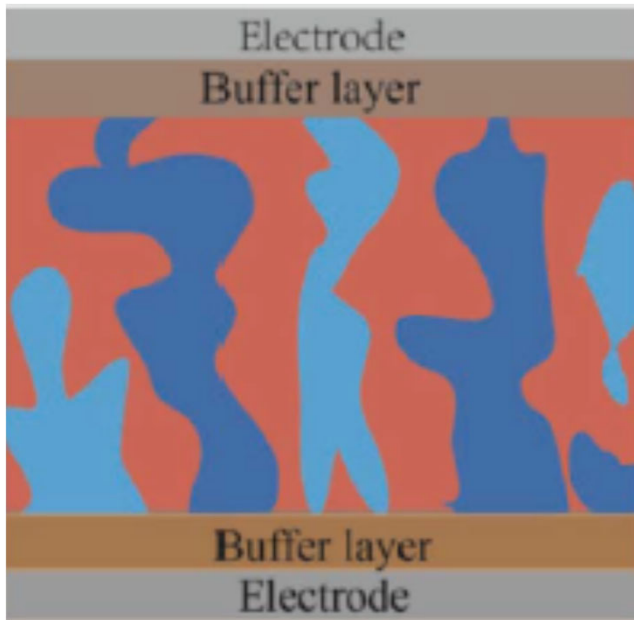


rr-P3HT



Example: material

Bulk heterojunctions in organic semiconductor solar cells



- Donor/acceptor interface is required to dissociate excitons in low dielectric constant semiconductors
- Energy difference between lowest unoccupied molecular orbitals (LUMO) of the donor and the acceptor provide the driving force for exciton separation
- Exciton diffusion length is only 10-20 nm so only the excitons generated near donor/acceptor interface can be separated

Preparation of ultrathin films

Terminology for ultrathin films

Continuous film,
or closed film



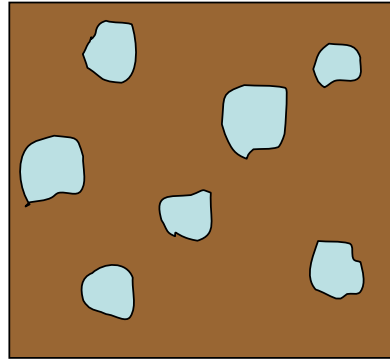
Smooth
surface

- Surface force studies
- Adsorption studies etc.

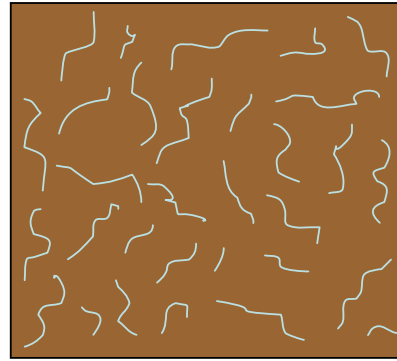


**The effect of morphology
as small as possible.**

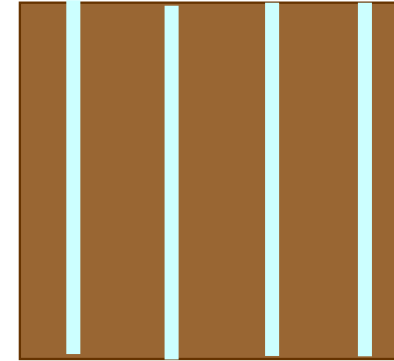
Discontinuous film
– islands



Discontinuous film
– molecules



Discontinuous film
– patterned structures



■ substrate
■ coating

Distinct morphology

- Visualising different phenomena:
 - association
 - degradation etc.



**Distinct morphology yields distinct
changes in morphology.**

Methods of preparation

Conventional, commonplace and robust

Langmuir-Blodgett deposition
Spin coating

Nanolithography
Soft lithography

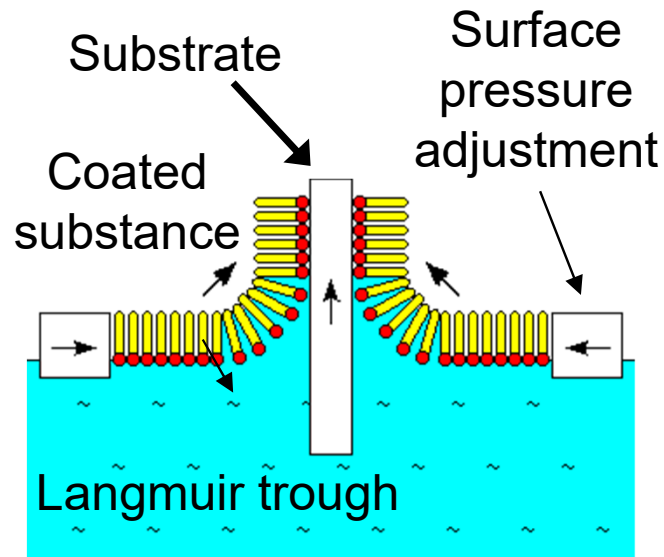
Chemical vapour deposition

Electrophoretic deposition

Self assembly:

- self assembled monolayers (SAM)
- convective self assembly
- hierarchal self organisation
- layer-by-layer deposition
- polymer brushes

Langmuir-Blodgett deposition

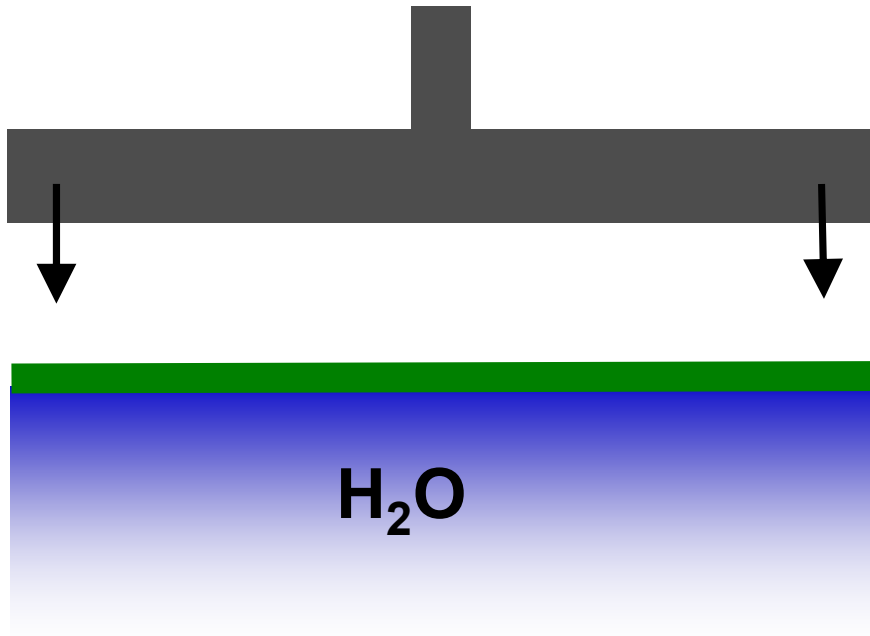


LB-deposition of surfactant

- (1) The film-forming compound is dissolved and spread on liquid in a Langmuir trough
- (2) The solvent is allowed to evaporate
- (3) Surface pressure is adjusted to form a monolayer of coated substance on the liquid
- (4) A substrate is dipped through the monolayer
- (5) The coated substance organises on the substrate
- (6) The dipping may be performed multiple times; each time a monolayer is deposited

Langmuir-Schaefer deposition

Exactly like LB deposition but the substrate is aligned horizontally, not vertically.

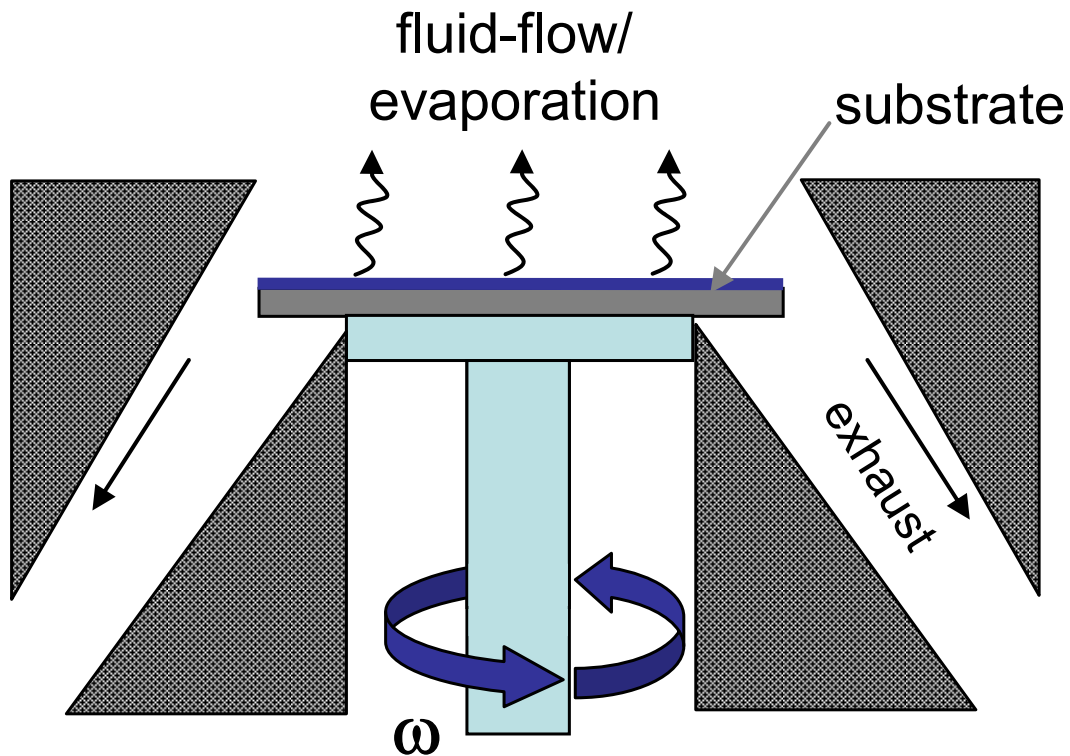


LS deposition is used when attachment of the film is desired exclusively on one side of the substrate (e.g., with substrates for quartz crystal microbalance)

Spin coating

Casting a film from solution:

- the solvent is removed by high speed spinning (ca. 1000-10000 rpm)



Chemical vapour deposition

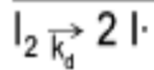
- A gaseous precursor reacts or decomposes on the substrate
- Widely used in semiconductor industry (inorganics)
- Incorporates several subspecies, such as Atomic Layer Deposition, Direct Liquid Injection etc.

For polymer films: Initiated Chemical Vapor Deposition (iCVD)

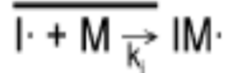
Initiated CVD

- Initiator and monomer species are vaporised
- Heated filament wires thermally dissociate the initiator
→ Radicals are created for initiation
- Substrate is backside-cooled

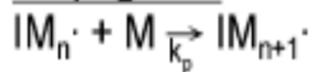
Radical generation (gas phase/filament)



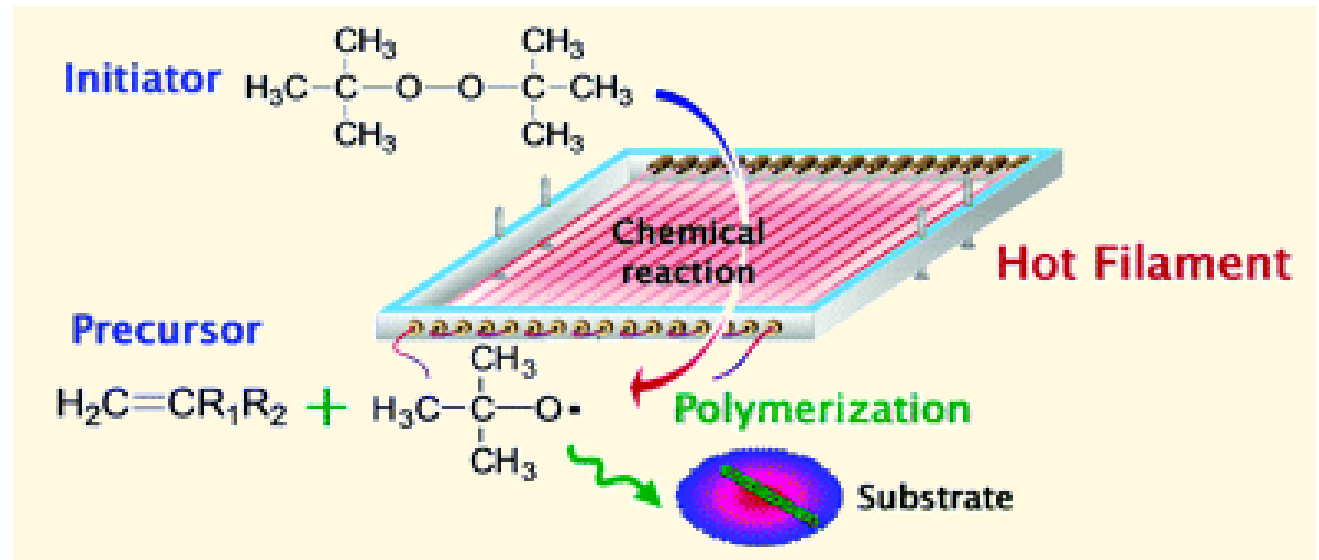
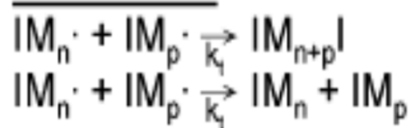
Initiation



Propagation



Termination



Nanolithography and soft lithography

Some examples:

(I) Photolithography:

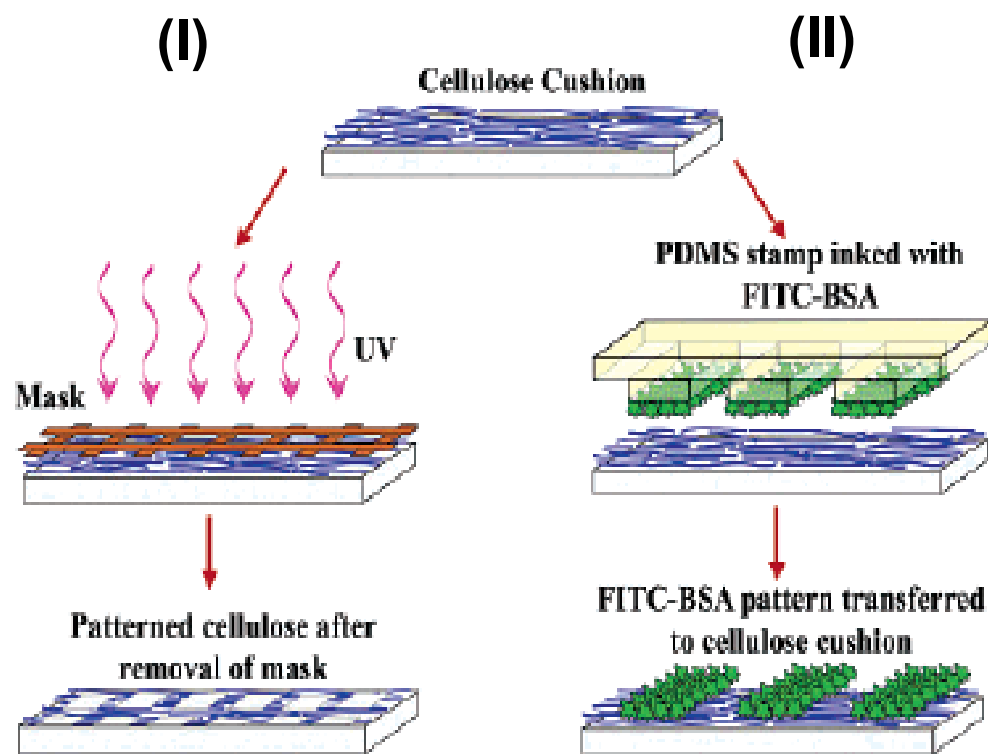
The film is patterned by using a mask and by removing the susceptible areas with, e.g., light or UV-light.

(II) Soft lithography:

A small “stamp” is used to prepare micron-sized patterns on a film or a substrate.

Review on soft lithography:

Adv. Funct. Mater. **2010**, 20, 3411.



Polymer brushes

Definition:

- An assembly of polymer chains which are tethered by one end to a surface

Preparation:

(I) “Grafting to” approach:

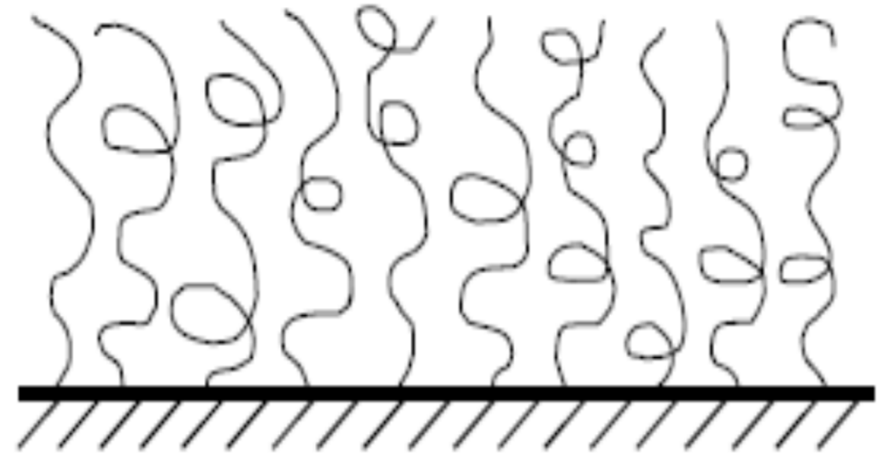
- end-functionalized polymer is attached to the receptive surface

(II) “Grafting from” approach:

- polymer is polymerized *in situ* from an initiator at the surface

(III) Physisorption:

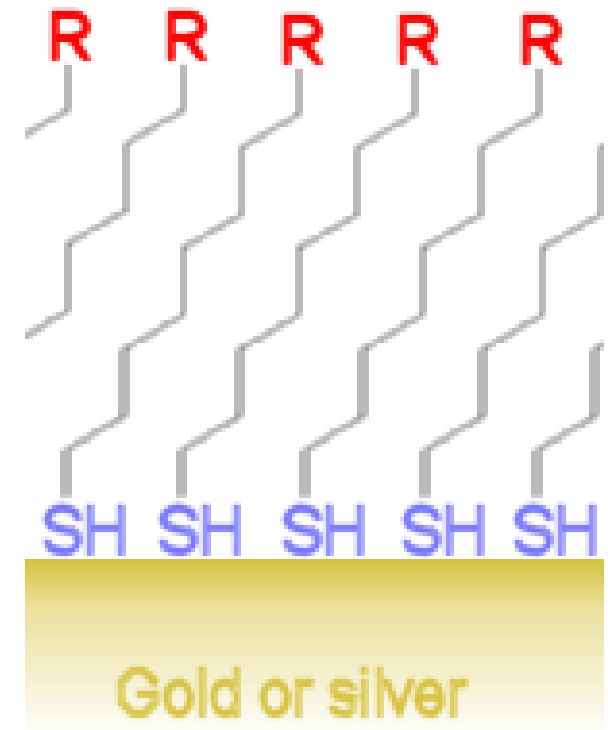
- (for block copolymers): one block adsorbs on the surface



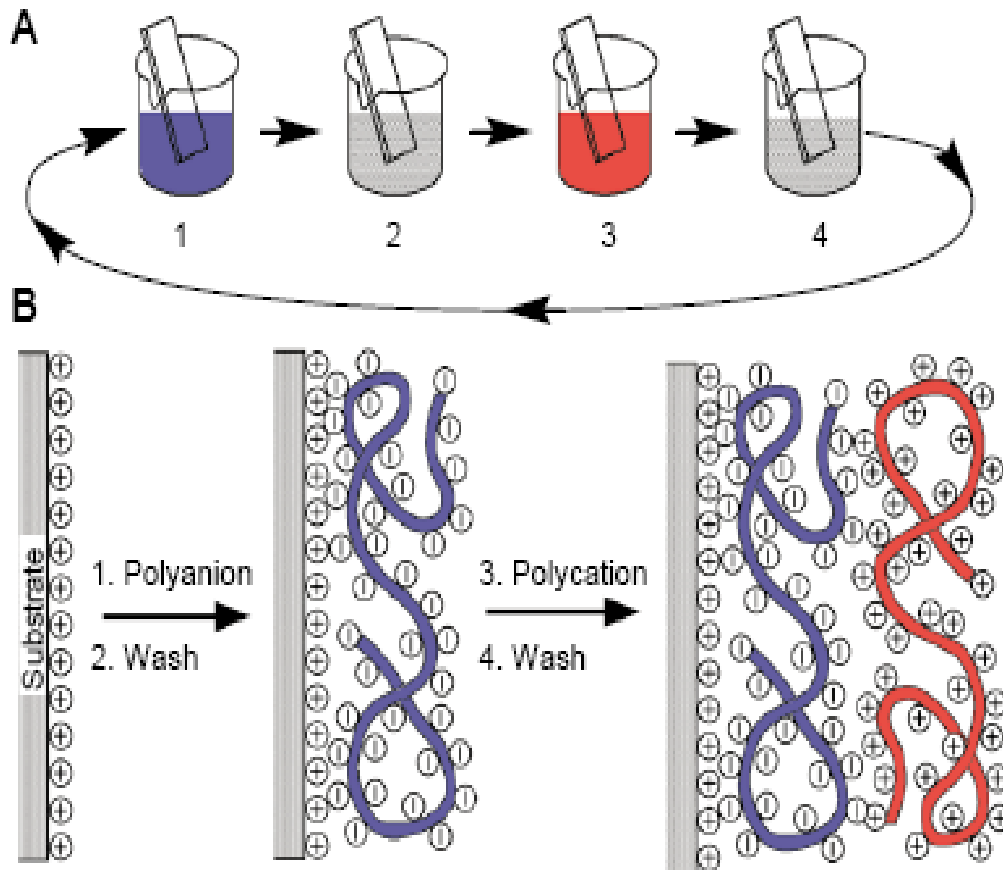
Review on polymer brushes:
J. Mater. Chem. **2010**, 20, 4981.
Chem. Rev. **2014**, 114, 10976.

Self-assembled monolayers (SAM)

- Preparation utilises a strong chemical interaction between the surface and monolayer molecule
- Most common example: thiols on gold produce a uniform, well defined monolayer because of the strong attraction between Au and -SH.
- SAMs are often used as templates for thin film preparation for, e.g., polymer films

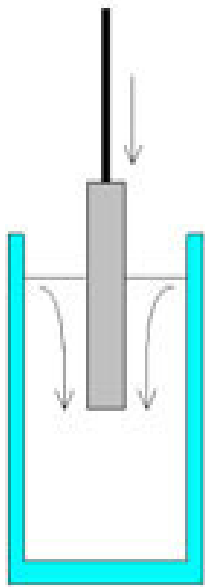


Layer-by-layer (LbL) deposition

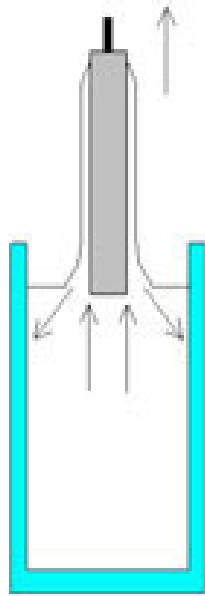


- Polyelectrolytes of opposite charges can be deposited one after another
- Experimentally the “easiest” technique: requires only polyelectrolyte solutions and washing in between
- Can be time-consuming
- Specific devices exist for LbL

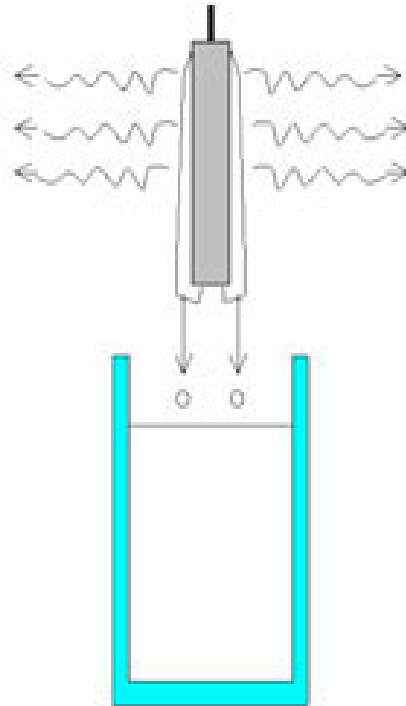
Dip coating



dipping



wet layer formation



solvent evaporation

- Substrate is dipped in a trough and dragged out with controlled speed
- Viscous drag, capillary forces, and evaporation control the film thickness
- Thickness may be uneven (wedge effect)

Dip coating vs. adsorption

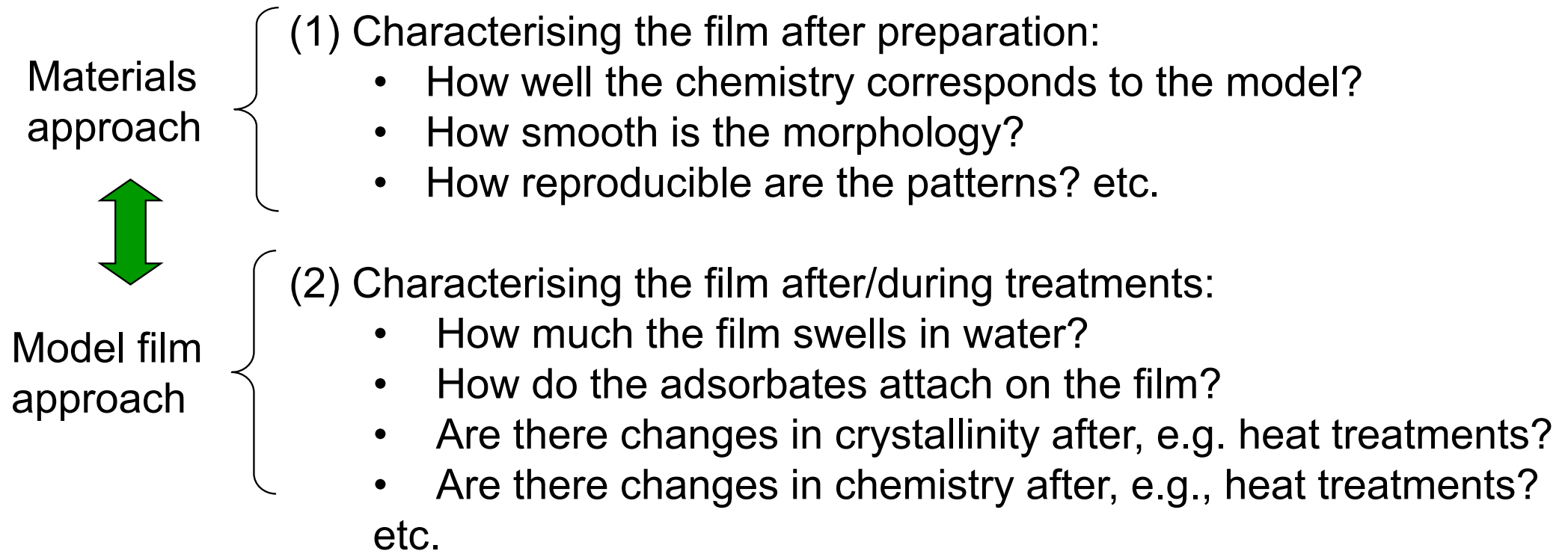
NOTE!

- Adsorption means enrichment of material on a surface by thermodynamic drive
- Adsorption can be used as a tool for film (and submonolayer) deposition: “dipping” a substrate in a solution/dispersion and rinsing away the extra substance afterwards
- Depositing films via adsorption is often called “dip coating”; this is completely wrong (see, previous slide)

Characterization of ultrathin films

Characterization

The function of characterization is two-fold:



Microscopic techniques

Atomic Force Microscopy (AFM)

- The most common technique for visualisation
- Yields 3D information (smoothness, vertical size of patterns)
- High resolution (however, laterally the <10 nm dimensions are exaggerated)
- Enables surface force studies

Scanning Tunnelling Microscopy (STM)

- The highest resolution (sub-atomic scale)
- However, requires conductive samples and atomically smooth films

Scanning Electron Microscopy (SEM)

- Faster than AFM
- However, no 3D information and lower lateral resolution (down to ~ 2 nm with the most sensitive equipment)

Transmission Electron Microscopy (TEM)

- Very high lateral resolution
- However, requires <100 nm thick special substrate

Surface sensitive spectroscopies

X-ray Photoelectron Spectroscopy (XPS/ESCA)

- Requires ultra-high vacuum
- Chemical information from ~10 nm on the surface
- Distinguishes elements (bar hydrogen)
- Distinguishes oxidative states of elements
- Quantitative with precautions

Secondary Ion Mass Spectroscopy (SIMS)

- Requires ultra-high vacuum
- Mass spectroscopy selectively on the surface (< 2 nm on the surface)
- Polymer recognition requires Time of Flight (ToF) detector

Others: Ultraviolet Photoelectron Spectroscopy (UPS)

Auger Electron Spectroscopy

Surface sensitive IR such as ATR-IR

Surface sensitive spectroscopies

ESOTERIC ONES

High Resolution Electron Energy Loss Spectroscopy (EELS)

Low Energy Electron Diffraction Spectroscopy (LEEDS)

Extended X-ray Absorption Fine Structure (EXAFS)

Sum Frequency Generation (SFG)

NOTE: These techniques work mainly for (inorganic) single crystals
Example: atomically smooth Rhodium (110).

Surface sensitive spectroscopies

Surface sensitive variants of IR spectroscopy:

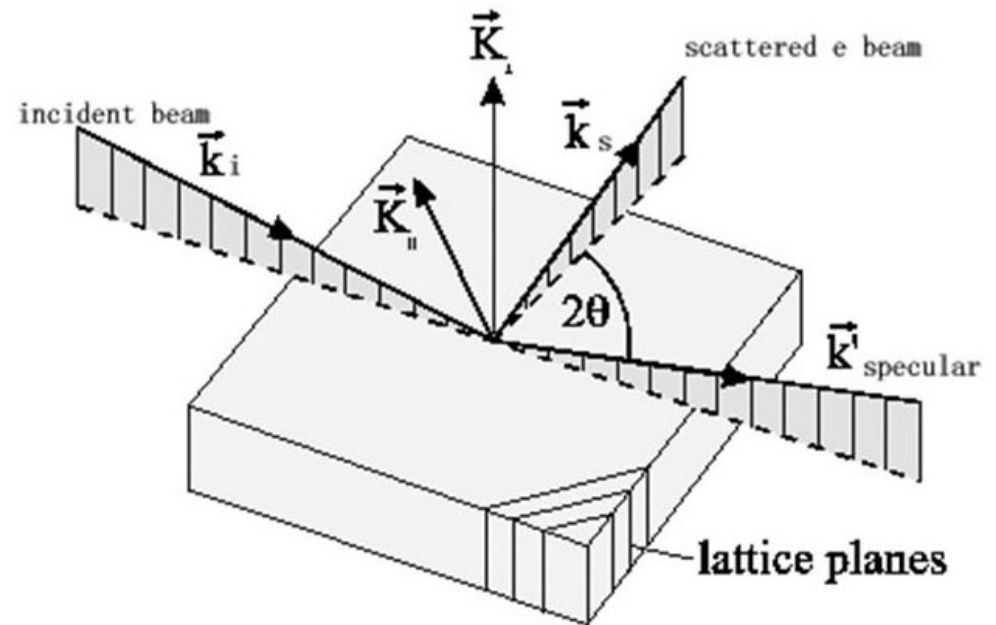
- Attenuated total reflectance infrared spectroscopy (ATR-IR)
- Reflection absorption infrared spectroscopy (RAIRS)

Surface sensitive variants of Raman spectroscopy

- Surface enhanced Raman spectroscopy (SERS)

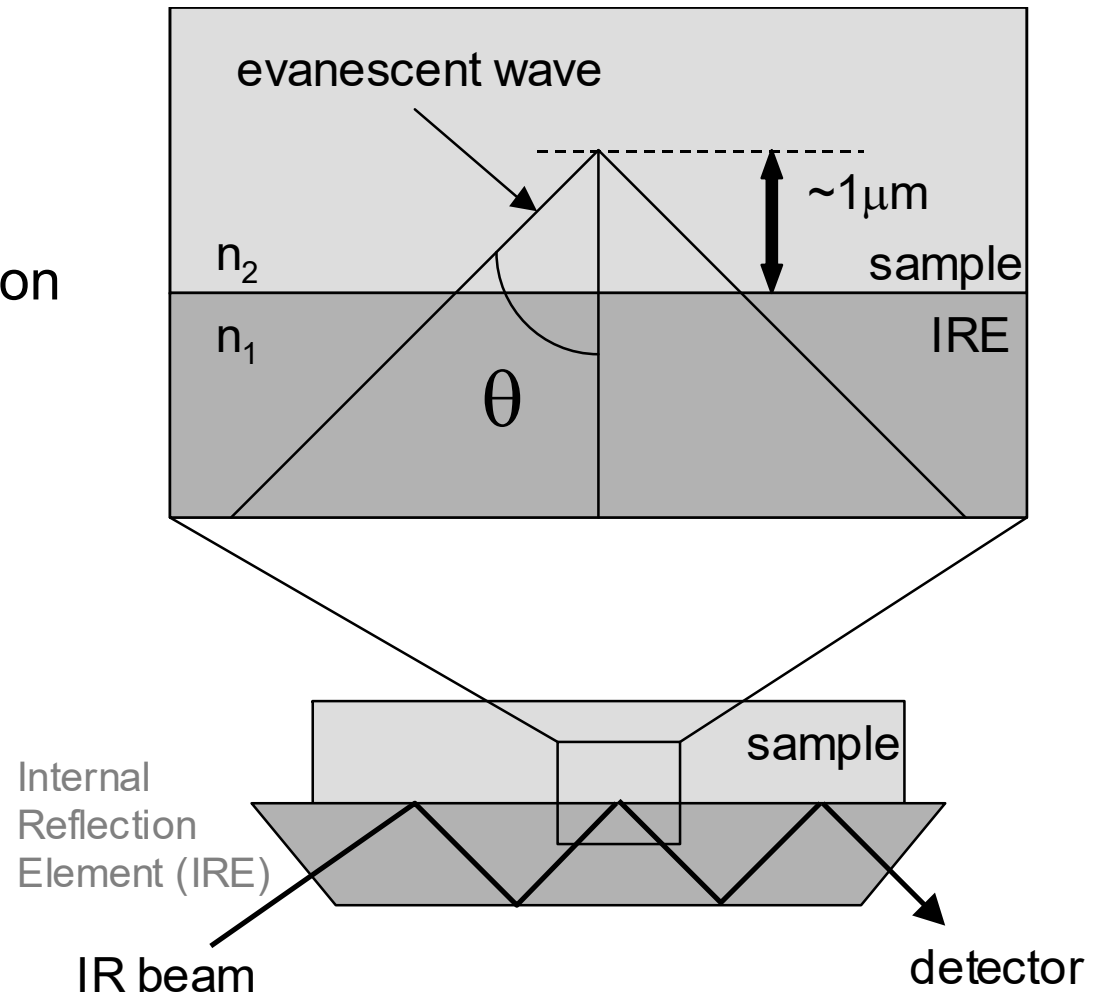
Surface sensitive scattering

- Surface sensitive X-ray scattering involves the use of grazing incidence (GI) angle (usually $1^\circ - 3^\circ$)
- Generally, soft polymer ultrathin films require the use of a synchrotron to enhance the intensity of the X-ray beam
- GI-WAXS, GI-SAXS



ATR-IR

- Common equipment
- Requires no sample preparation
- Surface sensitivity $\sim 1\ \mu\text{m}$



ATR-IR

- If the film is prepared on the ATR-crystal (internal reflection element), the ATR can be used to characterize thin films and even to study adsorption on it
→ Limited choice of substrates

ATR-IR cannot analyse an ultrathin film if:

- The substrate absorbs infrared radiation
OR
- The substrate is transparent to infrared radiation

ATR-IR can analyse an ultrathin film if:

- The substrate reflects infrared radiation
AND
- The substrate is soft enough to enable good contact between the sample and the ATR crystal

X-ray reflectivity

- Monitoring the intensity of X-rays, reflected by the sample at grazing angles

INFORMATION

- thickness of the film
- mass density of the film
- roughness of the film

- When synchrotron radiation is used, information on the molecular orientation of the film is feasible

Examples on usage for thin films:

Langmuir **2004**, 20, 6187.

Langmuir **2004**, 20, 1698.

Langmuir **2008**, 24, 12093.

J. Am. Chem. Soc. **2010**, 132, 3678.

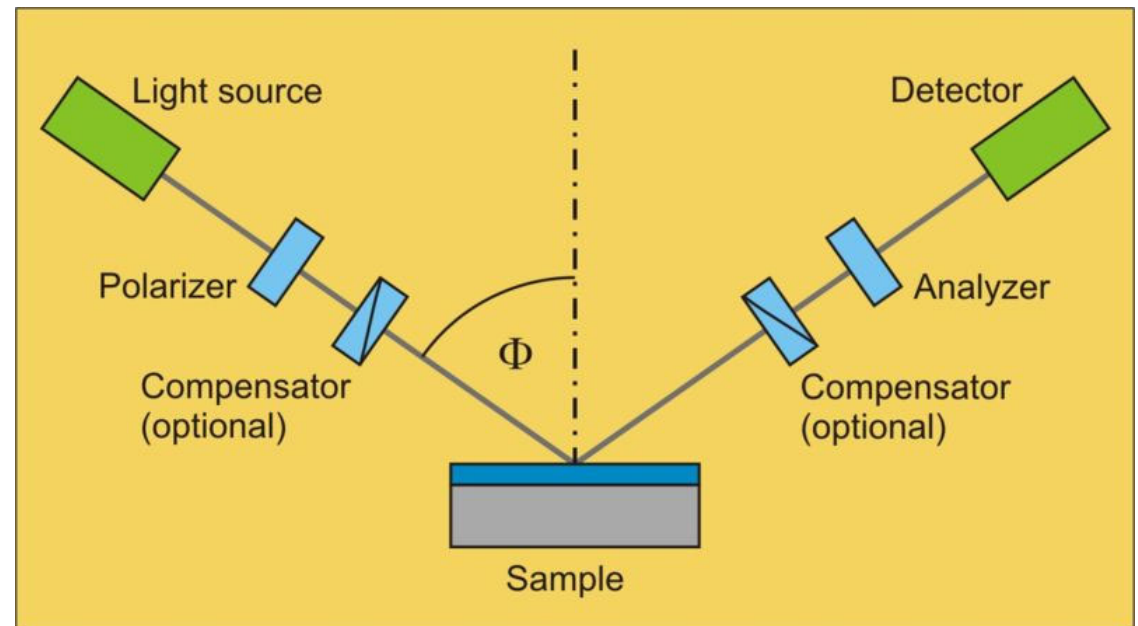
Langmuir **2017**, 33, 1295.

Ellipsometry

- Based on the change of polarisation of light which is reflected off the sample

INFORMATION

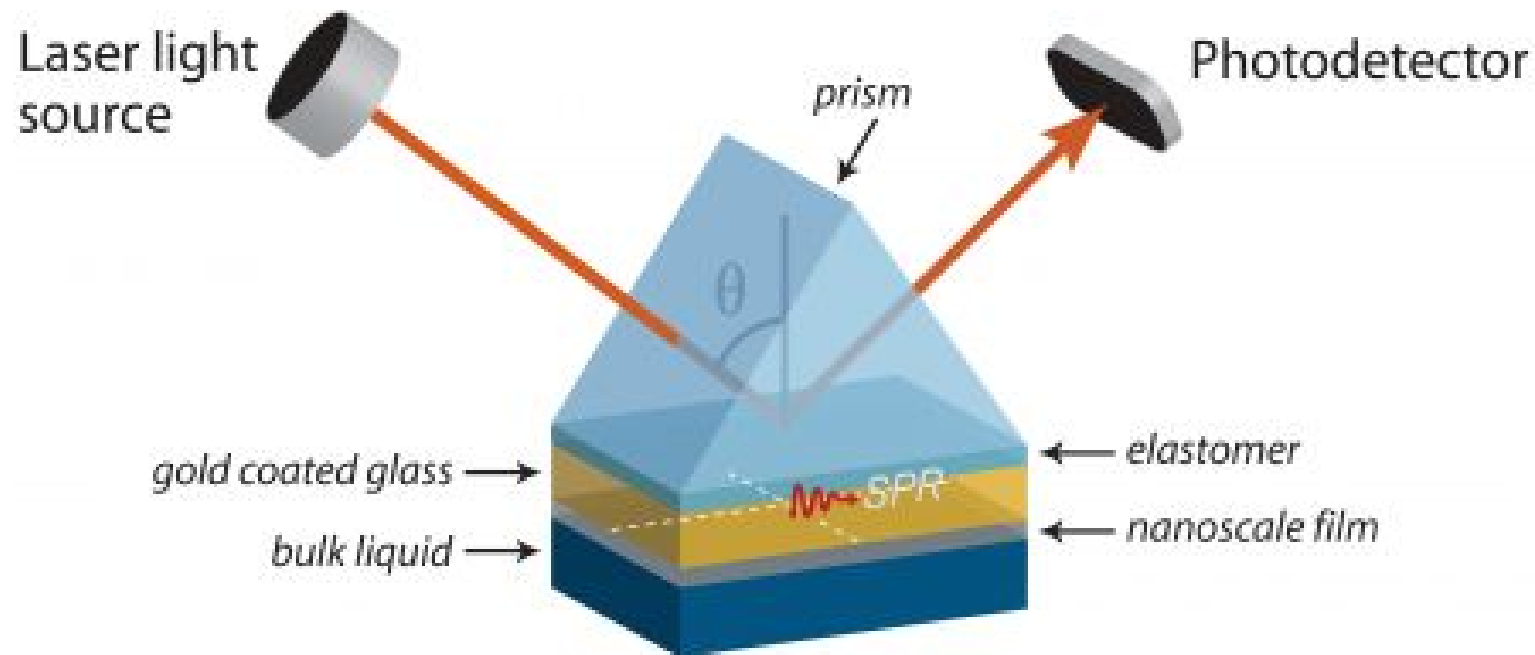
- thickness of the film
- refractive index of the film



- Can also be used in adsorption studies with thin films

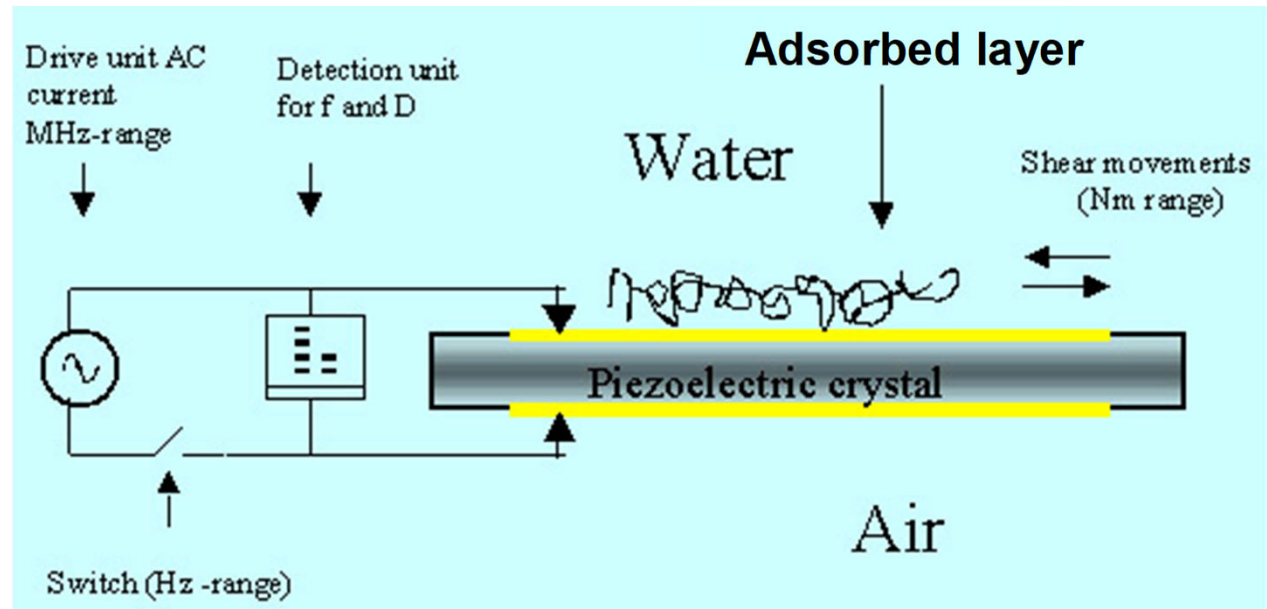
Surface plasmon resonance

- Light excitation causes the formation of plasmons on a metal surface
- The plasmons propagate on the metal-sample surface and are affected by the changes in the sample
- Enables *in situ* monitoring of, e.g., adsorption occurring on an ultrathin film



Quartz crystal microbalance (QCM)

- Frequency of the piezo-electric crystal changes when the mass changes
- Used mainly for adsorption studies



INFORMATION

- **Mass of the adsorbed layer**
- **Viscoelastic properties of the adsorbed layer**

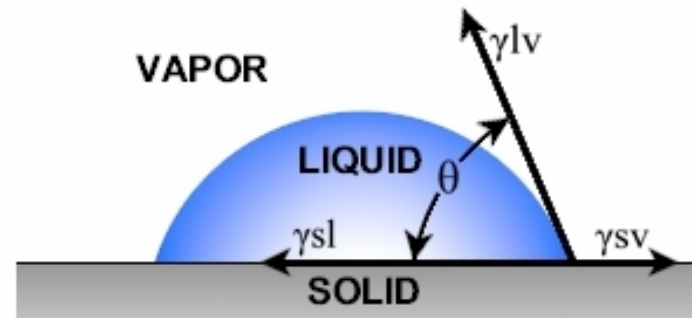
Contact angle with liquids

- Contact angle of water: hydrophilicity/hydrophobicity
- When measured with several solvents, surface energy of the film surface can be calculated (with precautions)

Chem. Rev. **1988**, 88, 927.

Young's Equation

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv} \cos \theta$$



θ is the contact angle

γ^{sl} is the solid/liquid interfacial free energy

γ^{sv} is the solid surface free energy

γ^{lv} is the liquid surface free energy

Characterization – summary

THE MOST COMMON TOOLS FOR CHARACTERIZING THE PREPARED FILMS

Morphology:

- Atomic Force Microscopy (AFM)

Chemistry:

- X-ray Photoelectron Spectroscopy (XPS)

Thickness:

- Ellipsometry
- X-ray Reflectivity (XRR)

Characterization – summary

THE MOST COMMON TOOLS FOR CHARACTERISING THE FILMS AFTER/DURING TREATMENTS

Adsorption studies

- Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D)

Swelling of the film

- QCM-D
- Ellipsometry

Morphology

- Atomic Force Microscopy (AFM)

Chemistry

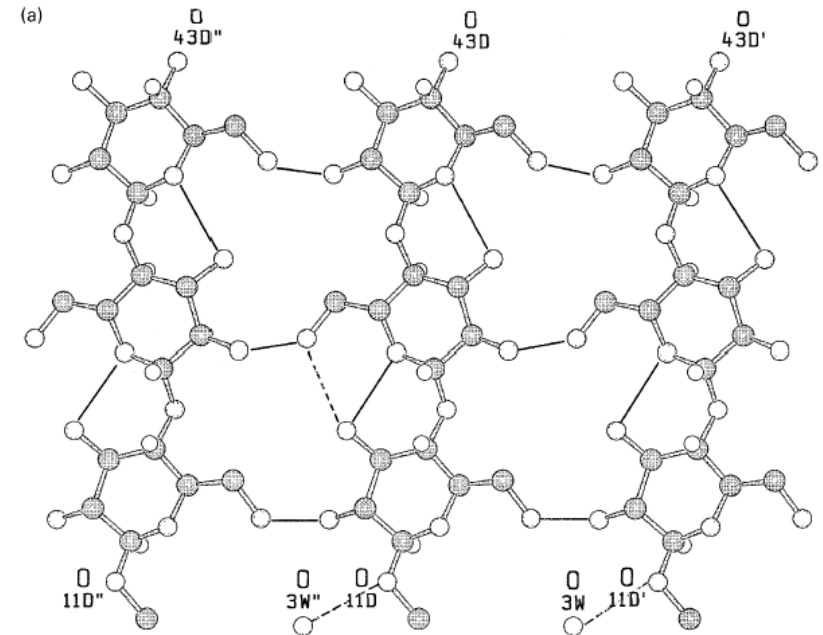
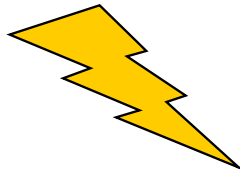
- X-ray Photoelectron Spectroscopy (XPS)
- Contact angle

**Example: ultrathin films of
cellulose explored by a means
of preparation and
characterization**

Personal account

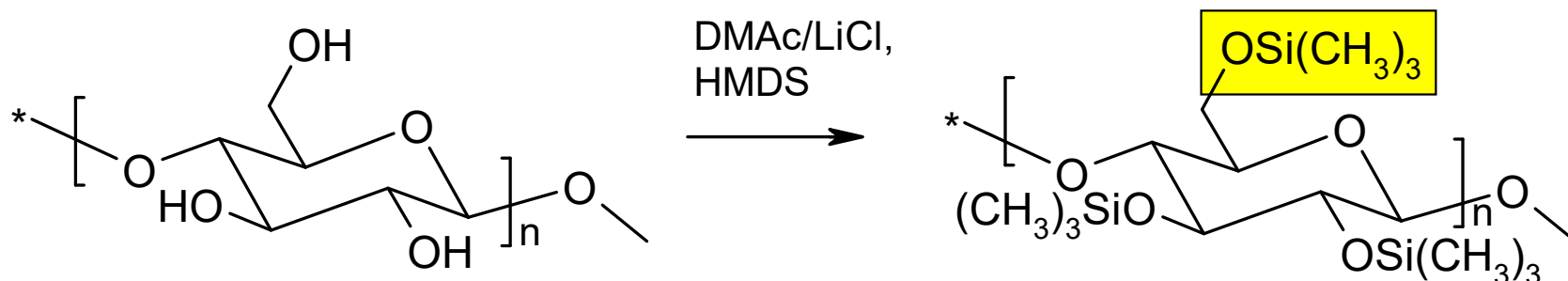
Initial difficulty with cellulose

- Cellulose is hydrophilic, yet it does not dissolve in water
- Solvents for cellulose are rather exotic and impractical, such as N-methyl-morpholine-N-oxide (NMMO) or LiCl in dimethylacetamide

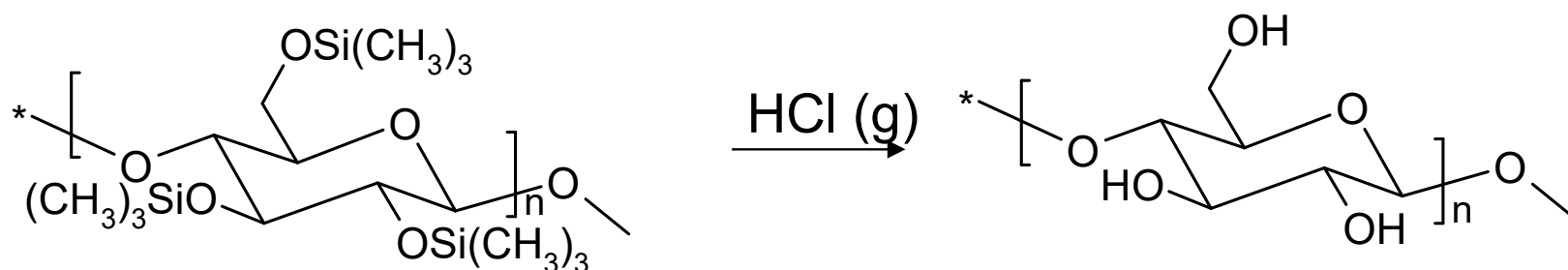


The essence of model surface preparation is generally making a dilute solution of the substance and coating it to a smooth substrate.

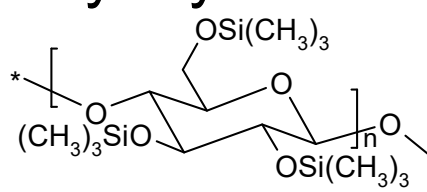
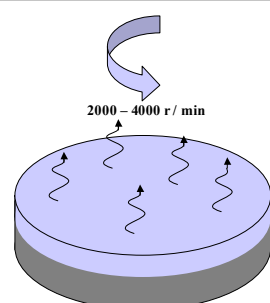
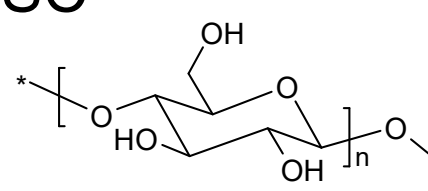
Introducing TMSC



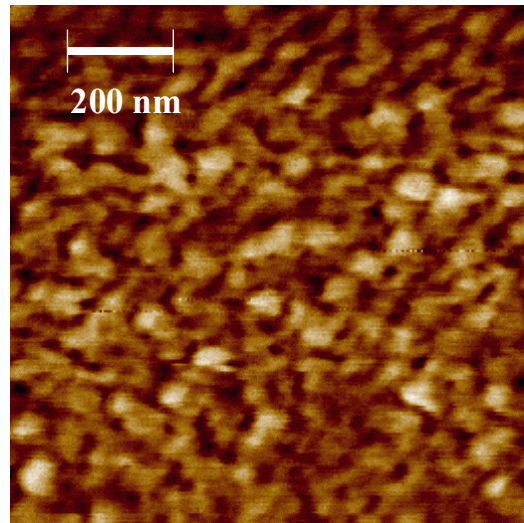
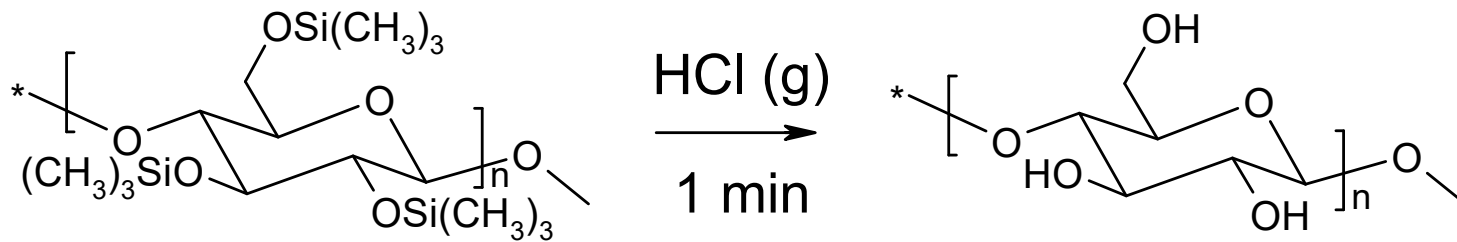
- Trimethylsilyl (TMS) group is introduced to cellulose forming trimethylsilyl cellulose (**TMSC**)
- Synthesised TMSC dissolves easily to common non-polar solvents
- Silyl ethers are unstable and easy to cleave with aqueous base or acid



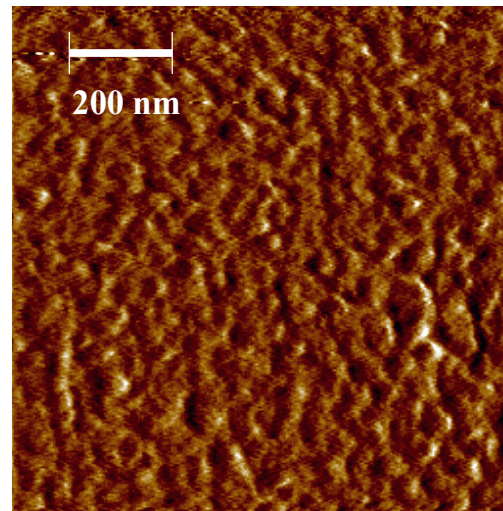
Protocol for spin coating TMSC

Part I	Preparation of trimethylsilyl cellulose (TMSC) 	Time 3 days	Effects on the cellulose film Chemistry (DS of TMSC)
Part II	Spin coating on untreated silicon or gold 	1-2 min	Morphology
Part III	Hydrolysis of TMSC to cellulose 	1 min	Chemistry (extent of hydrolysis)

Hydrolysis of TMSC to cellulose



TMSC



Cellulose

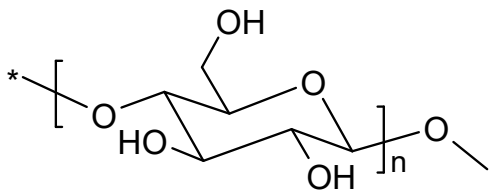
AFM images

- Hydrolysis of TMSC is not spontaneous
- However, within **one minute** TMSC is hydrolyzed back to cellulose with HCl in a **vapour phase** reaction at **room temperature**
- Chemical structure can be verified with XPS and ATR-IR, morphology with AFM

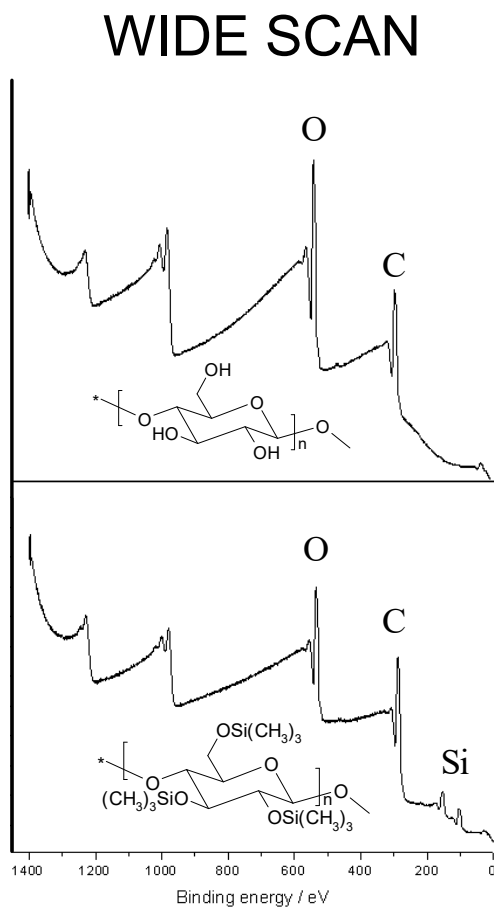
Film characterization by XPS

- X-ray photoelectron spectroscopy (XPS) probes first 10 nm of the surface

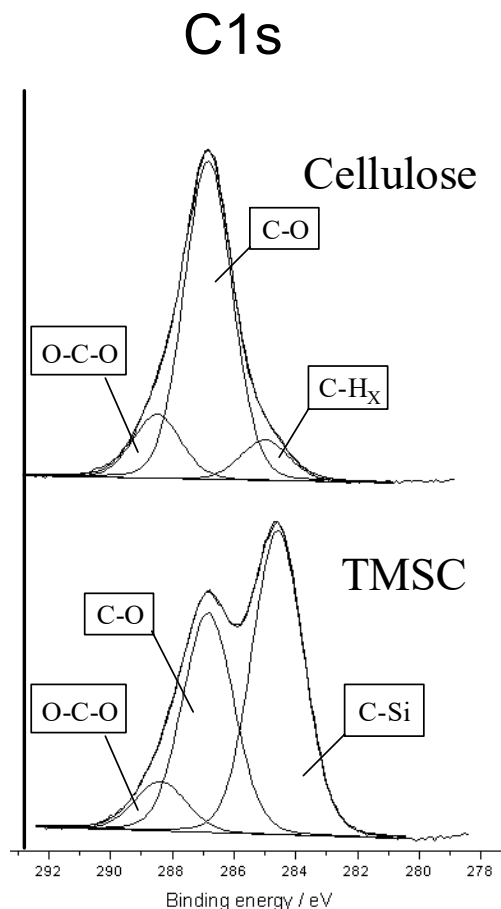
**Experimental:
O-C-O/C-O
= 0.21**



Theoretical: 0.20
(1 O-C-O in 5 C-O
bonds per
monomer)



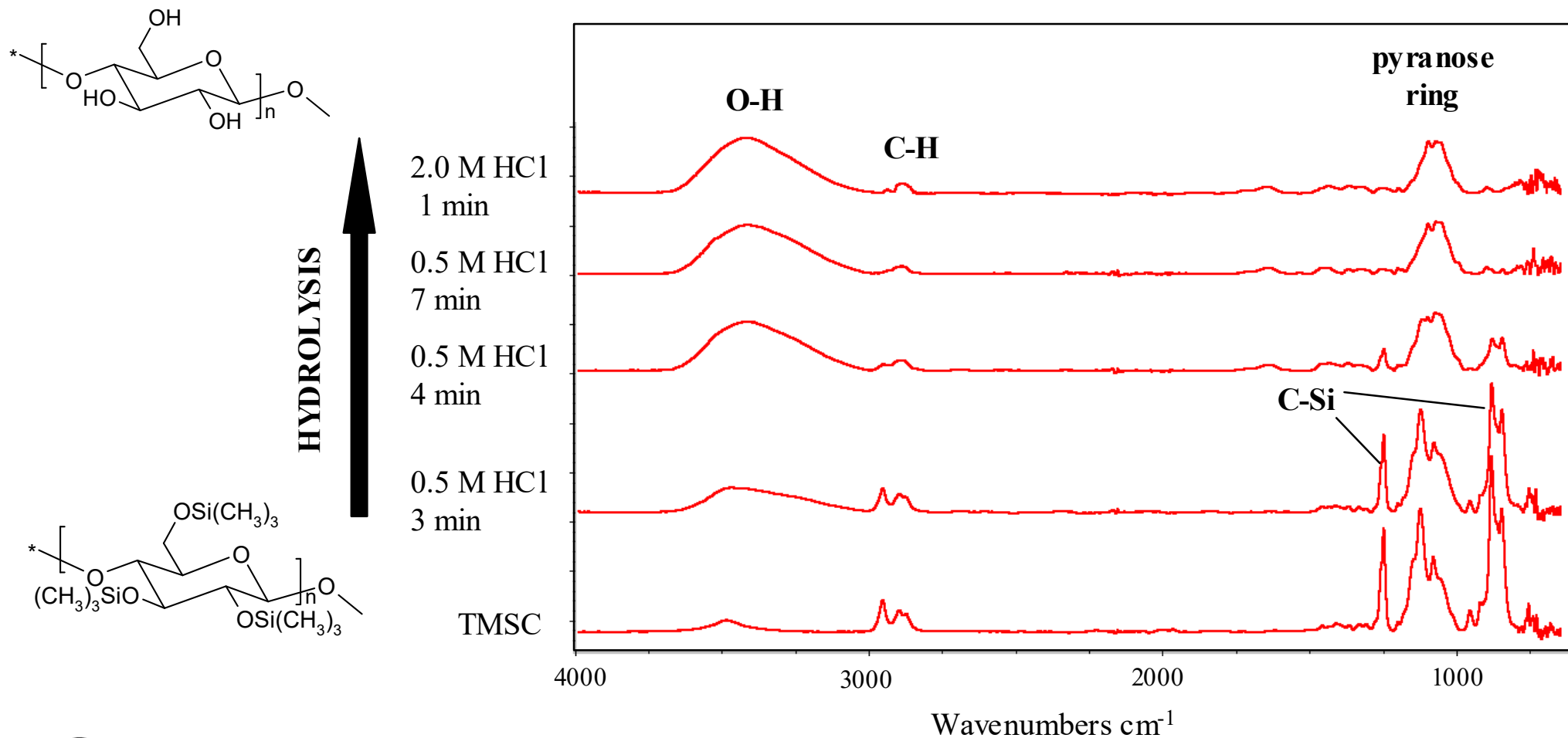
HYDROLYSIS, 2 M HCl for 1 min



Other characterization: ATR-IR?

- Initially, the cellulose films were prepared on a silicon substrate
- Problem: silicon is transparent to IR radiation (plus partially absorbs it) and it is a hard material
- Solution: prepare the films on gold (reflects IR radiation and is a soft material enabling good contact between the film and the ATR crystal)

ATR-IR analysis of TMSC→cellulose



After preparation of films...

What to do with it?

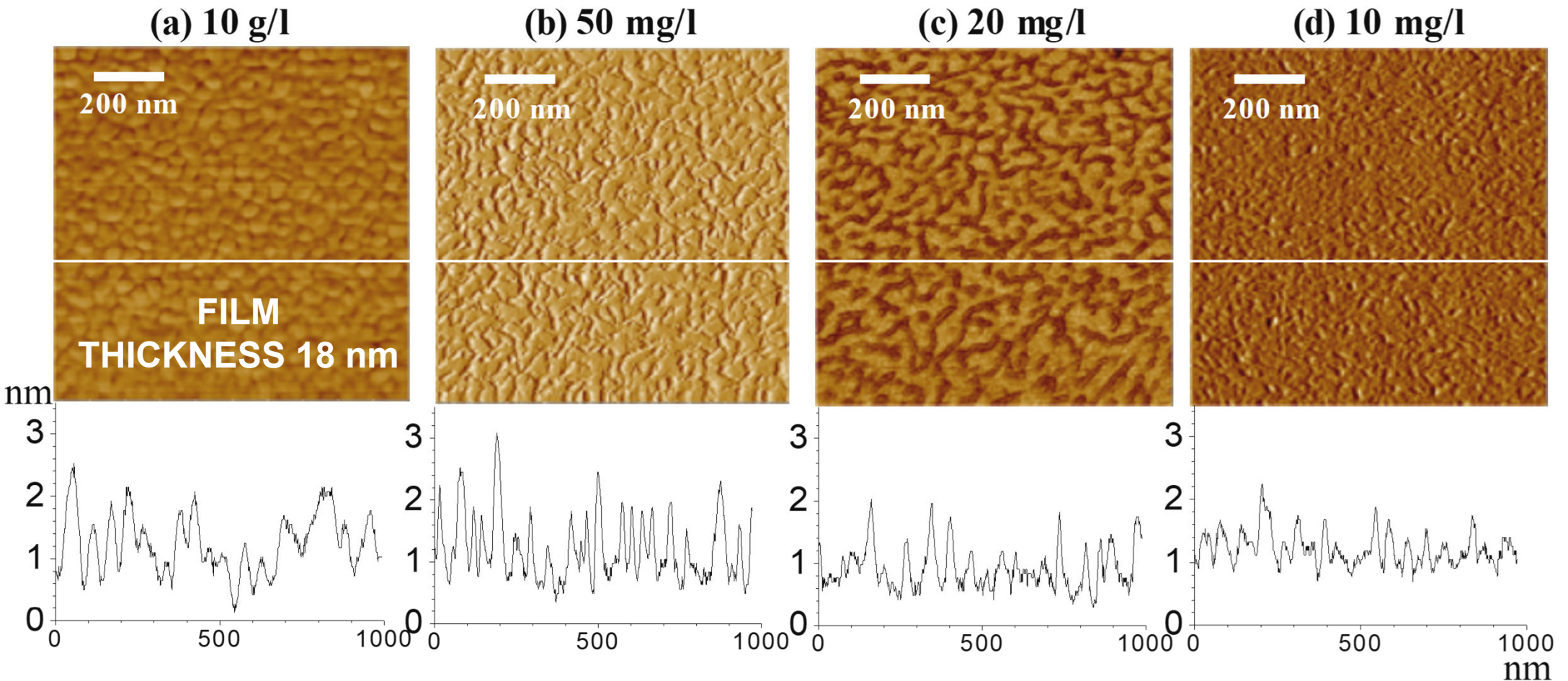
A lot of surface force and adsorption studies exist

How about morphological changes after simple treatments, like swelling in water?

Problem: the films are very smooth \leftrightarrow no morphological changes

Solution: induce morphology on the film by a different preparation technique

Submonolayers of cellulose

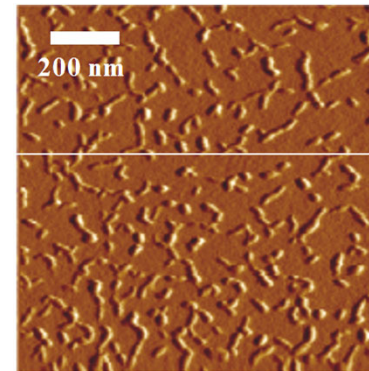
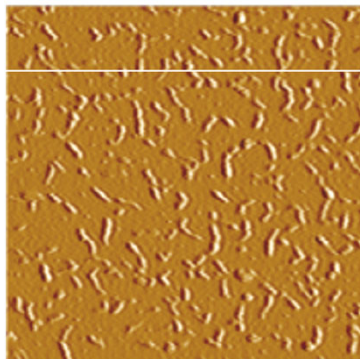
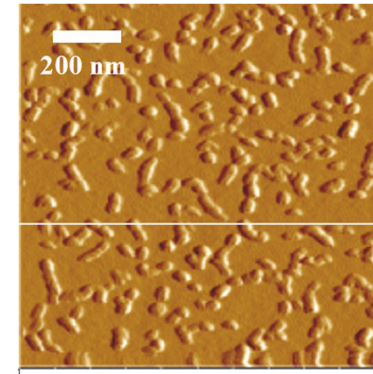
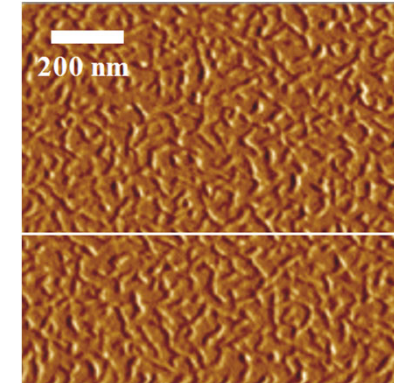
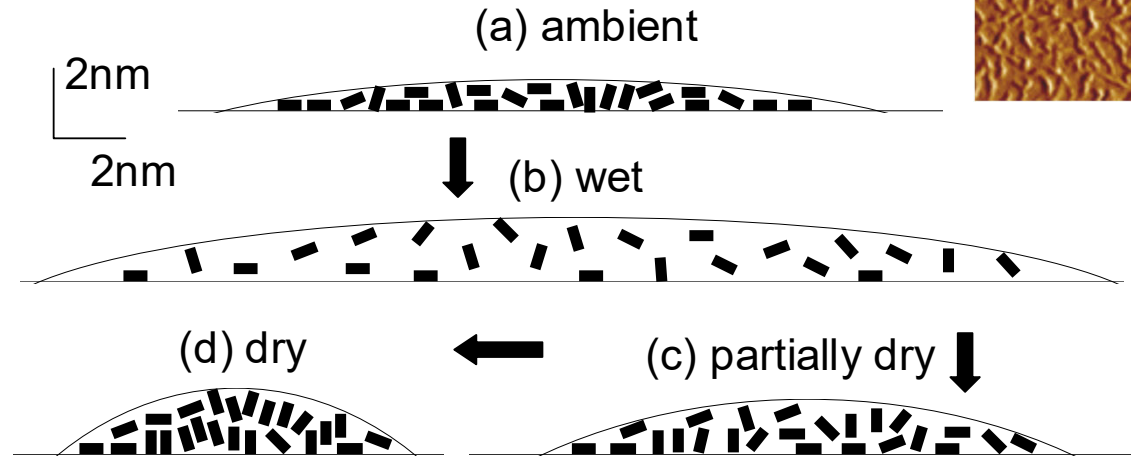


- Cellulose forms islands but they are longitudinal, i.e., fibre-like

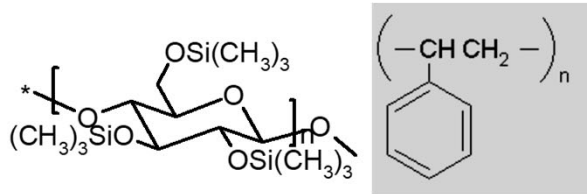
Swelling/drying

Irreversible changes in morphology upon wetting/drying were observed with AFM.

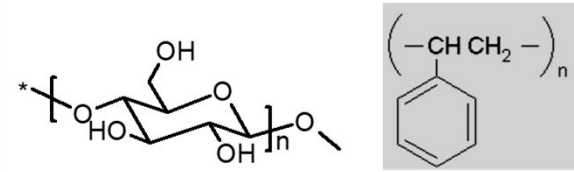
Schematic cross section of a single cellulose island



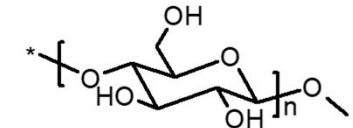
Blending TMSC with polystyrene



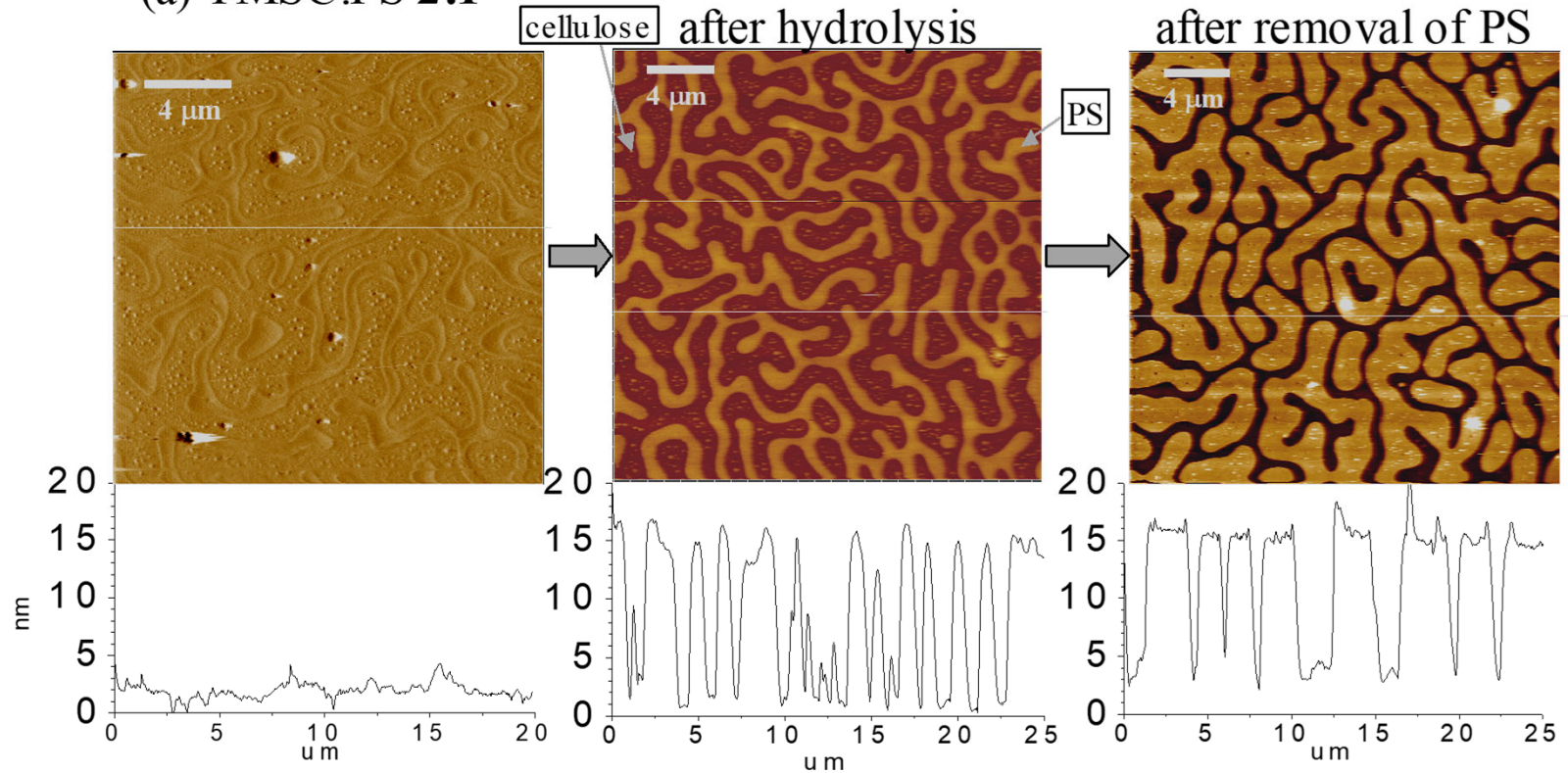
(a) TMSC:PS 2:1



(b) Cellulose:PS



(c) Cellulose only,
after removal of PS



Two phases are
equally high.

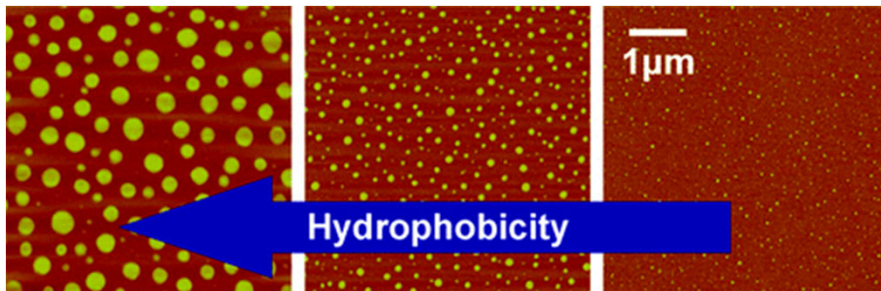
TMSC contracts as it
transforms to cellulose!

PS can be removed by any
non-polar solvent!

Macromolecules
2005, 38, 10712.

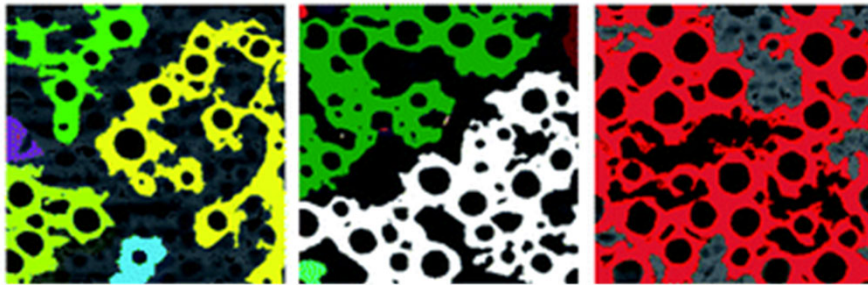
Further work with TMSC blends

Polystyrene: tunable hydrophobicity



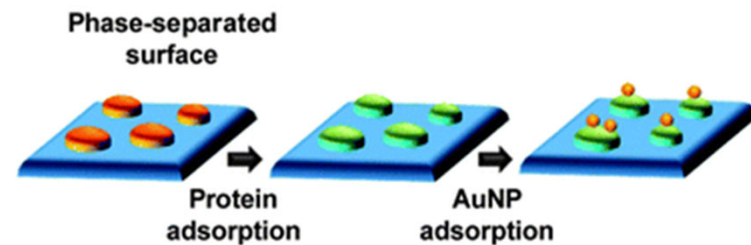
Taajamaa et al. *Biomacromolecules* **2009**, 10, 1276.

Cellulose acetate: phase-specific pores



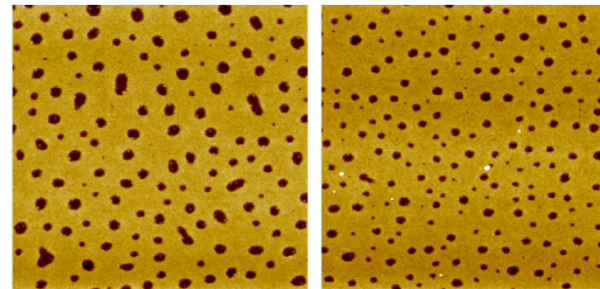
Taajamaa et al. *Soft Matter* **2011**, 7, 10386.

Polystyrene/BSA/gold nanoparticles



Taajamaa et al. *Chem. Commun.* **2013**, 49, 1318.

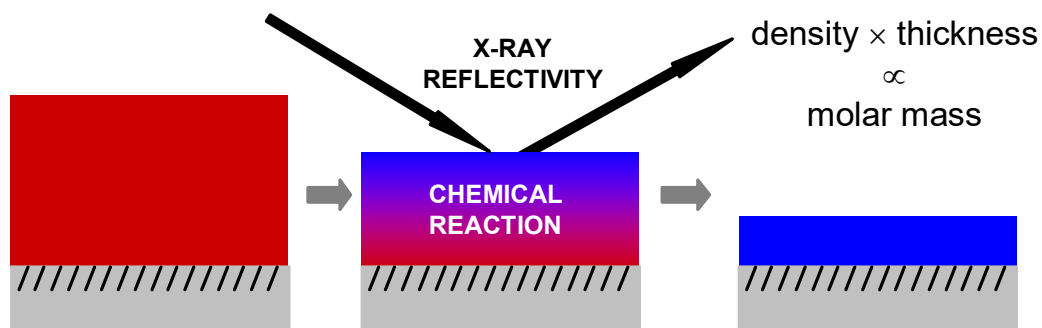
PMMA: cellulose-decorated nanocavities



Kontturi et al. *Soft Matter* **2009**, 5, 1786.

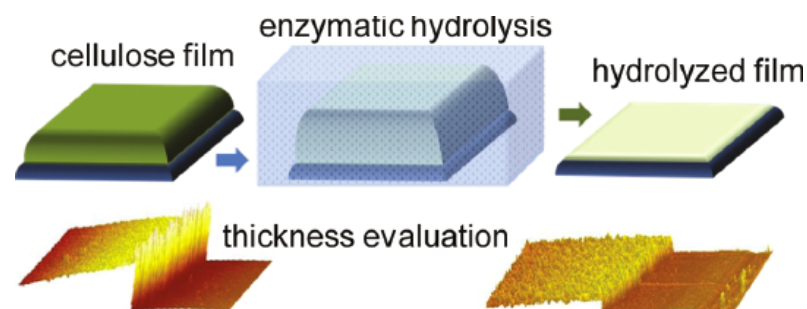
Platform for analytics

Following reaction kinetics within an ultrathin film

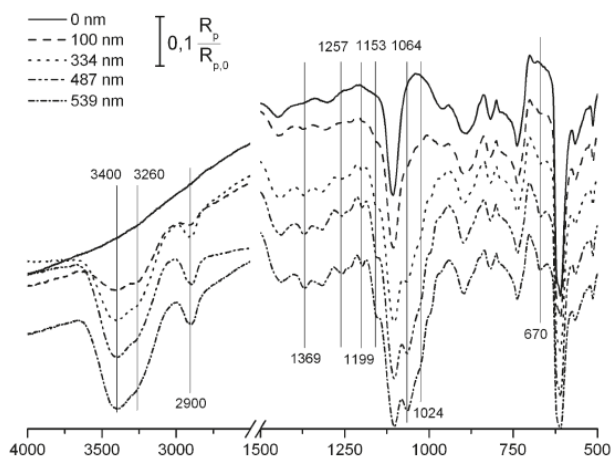


Kontturi and Lankinen *J. Am. Chem. Soc.* **2010**, 132, 3678.

Following enzymatic hydrolysis of monocomponent (amorphous) cellulose with quartz crystal microbalance



Suchy, Linder, Tammelin, Campbell, Vuorinen, Kontturi *Langmuir* **2011**, 27, 8819.



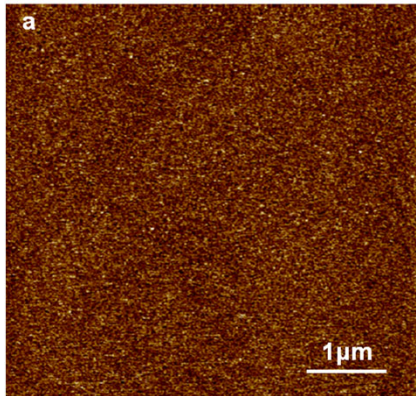
Thickness dependence of polymer films in reflection absorption infrared spectroscopy

Djak, Gilli, Kontturi, Schennach *Macromolecules* **2011**, 44, 1775.

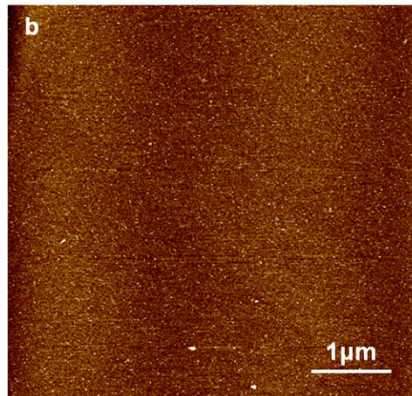
Fractal formation

Monolayers of trimethylsilyl cellulose on different substrates
Langmuir-Blodgett casting

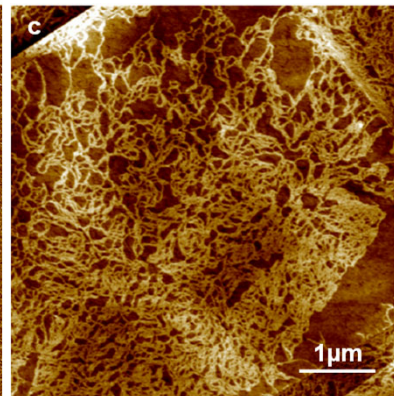
Substrate:
silica



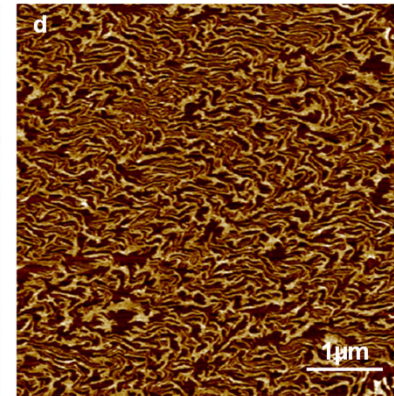
Substrate:
mica



Substrate:
graphite



Substrate:
methylated silica



Fractals
possess the
highest degree
of entropy in 2D

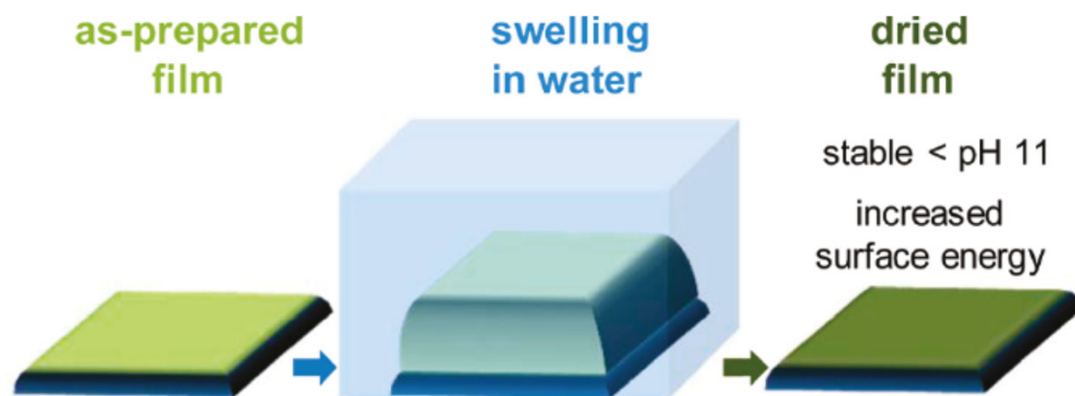
Decreasing order of surface energy

Entropy grows when surface energy decreases

$$T(dS) = dU - (\gamma_n)dA - \sum \mu_i dn_i$$

Further characterization

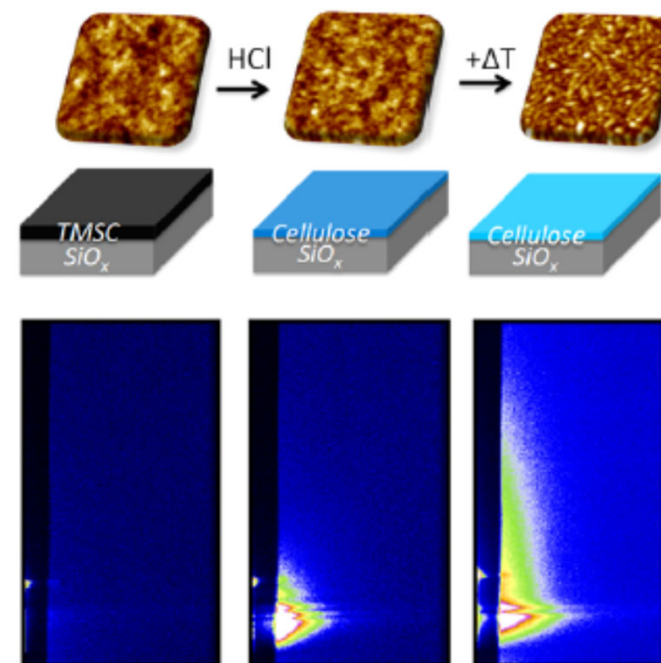
Characterization by GI-XRD and neutron reflectivity
Establishing a “stable amorphous cellulose film”



Kontturi et al. *Biomacromolecules* **2011**, 12, 770.

Characterization by GI-SAXS
Rearrangements upon annihilation

GISAXS *in situ* regeneration

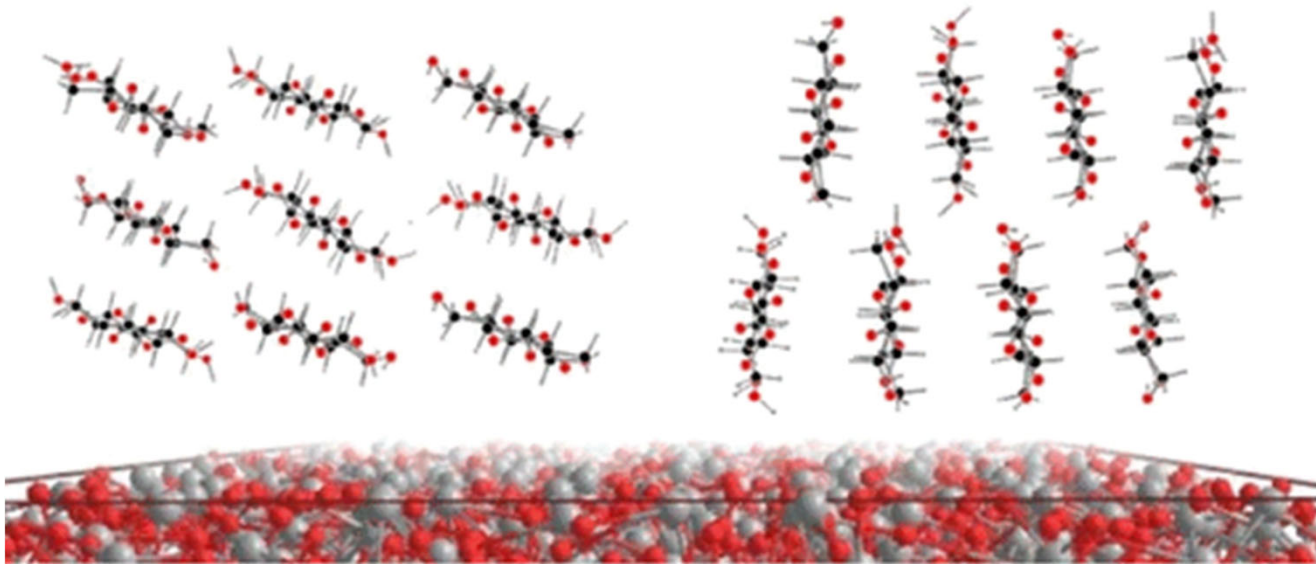


Ehmann et al. *ACS Macro Lett.* **2015**, 12, 770.

Further characterization

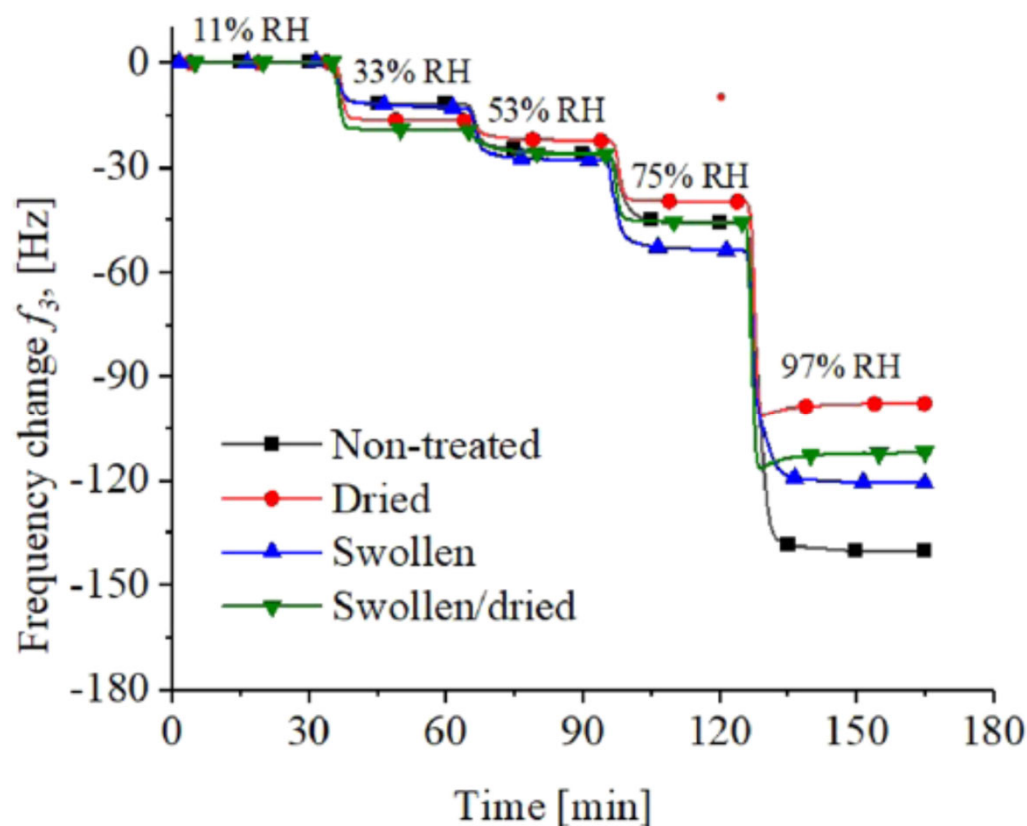
Characterization of thicker amorphous films by GI-XRD
A minor degree of order was found

Cellulose Thin Film Order



Kontturi et al. *Biomacromolecules* **2020**, 2, 653.

Humidity response

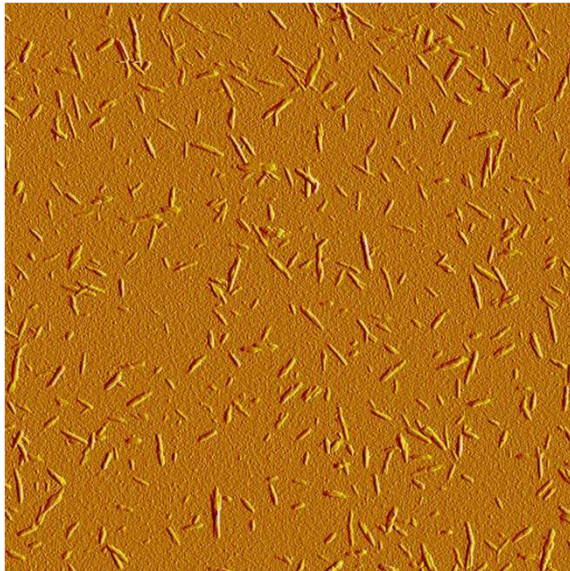


- Water vapor uptake was monitored by XRR and QCM-D on amorphous cellulose films
- Drying had a major impact on the water uptake

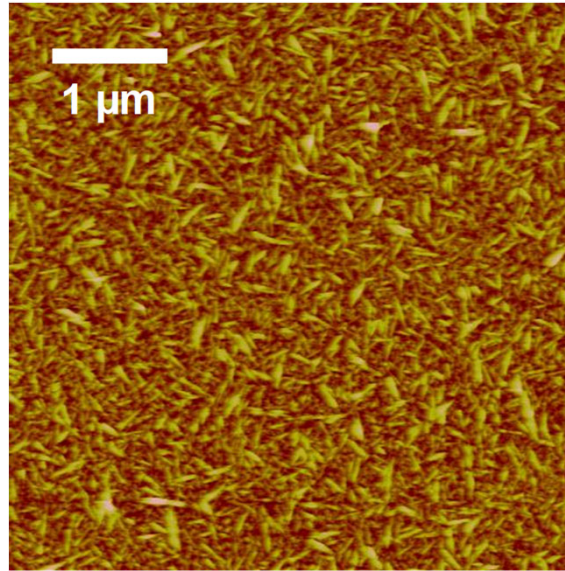
Cellulose nanocrystal films

Cellulose nanocrystals on different supports

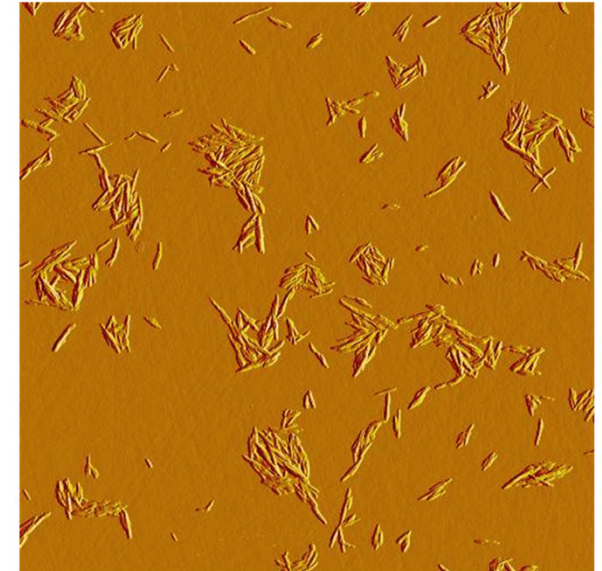
Cellulose
nanocrystals
on titania



Cellulose
nanocrystals
on amorphous
cellulose

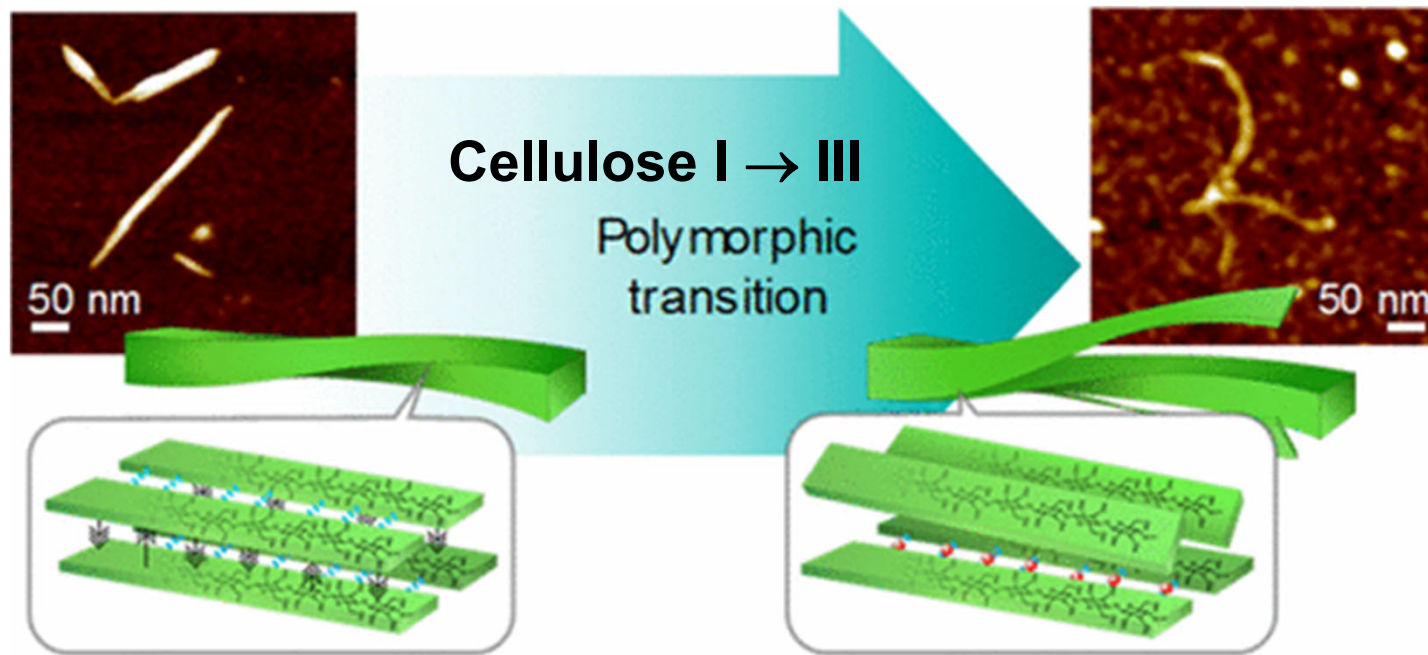


Cellulose
nanocrystals
on silica

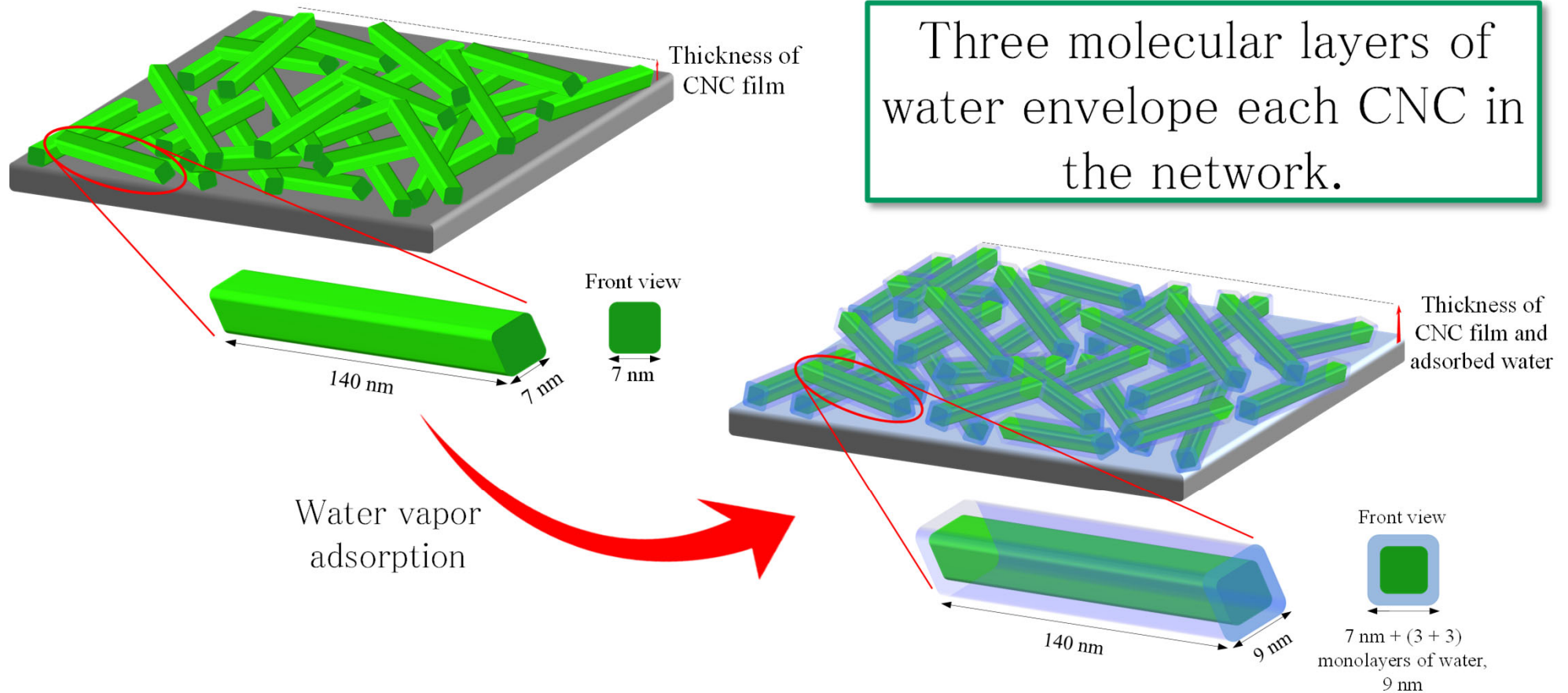


Exfoliation of cellulose nanocrystals

When nanocrystals are fixed on a surface, polymorphic transition from cellulose I to cellulose III is frustrated and exfoliation of the crystal occurs.

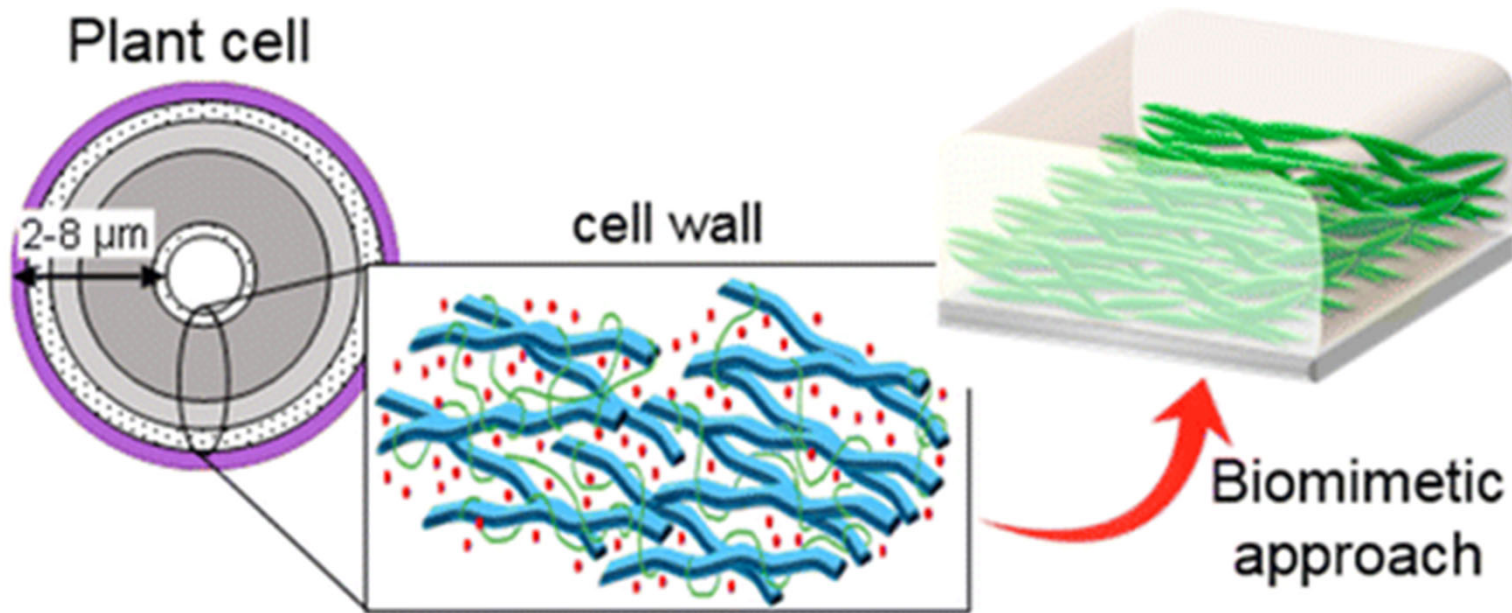


Swelling of CNC thin films

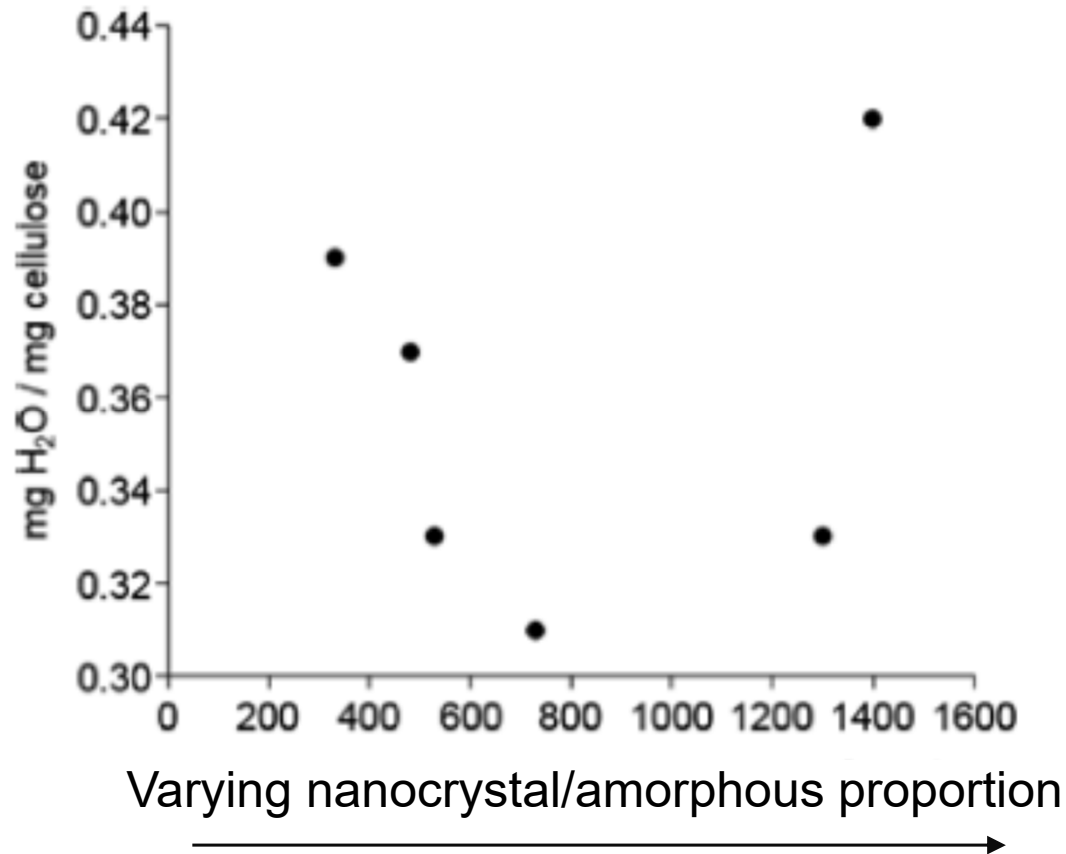


CNC/amorphous cellulose films

- Mix cellulose nanocrystals with an amorphous polysaccharide on a film
- Akin to the environment in the plant cell



CNC/amorphous cellulose films



- Water uptake is highly unexpected: it does not scale with nanocrystal/amorphous ratio
 - By varying nanocrystal/amorphous ratio, susceptibility to water can be controlled
- Only fundamental research can reveal the reasons behind the illogical water uptake

Summary

- Model films model both chemistry and morphology
- Sometimes totally smooth morphology is required (surface force studies, adsorption studies)
- Sometimes nanoscale morphology is favoured in order to see changes upon various treatments

Preparation in short

- Casting films from a solution by Langmuir-Blodgett deposition or spin coating

Characterisation in short

- Atomic Force Microscopy (AFM) – morphology
- Ellipsometry, XRR - Thickness
- X-ray Photoelectron Spectroscopy (XPS) – chemical composition