Laser based Processes for Thin Film Deposition

Thomas Lippert
Materials Group, Paul Scherrer Institut and
Laboratory of Inorganic Chemistry, ETH Zurich
thomas.lippert@psi.ch
http://www.psi.ch/materials

Thanks to...

- Group members (present and past, seniors and PhD students): A. Wokaun, C. W. Schneider, D. Pergolesi, A. Palla-Papavlu, D. Stender, T. Mattle, J. Chen, M. Pichler, S. Temmel, A. Ojeda, M. Bator, Y. Hu, J. Shaw-Stewart, R. Fardel, F. Simmen, I. Marozau, S. Canulescu, L. Urech, M. Montenegro, T. Dumont, M. Kuhnke, M. Hauer, G. Kopitkovas, D. O'Mahony, etc.)
- PSI colleagues: C. Niedermayer, M. Kenzelmann, T. Schmidt, R. Kötz, C. Conder, C. Borca, J. Stahn, H. Lütkens, P. Novak, etc.
- From other places: ETH, Empa, INFLPR, CNRS, CNR, Microsens, Imperial College, DTU, TCD, etc.
- Funding from SNF, CCMX, EU, PSI, etc.

Outline

- Introduction: laser based material transfer
- Laser transfer of oxides for energy applications: PLD (pulsed laser deposition)
- Laser transfer of sensitive and/or organic materials: LIFT (laser induced forward transfer)
- LIBWE (laser-induced backside wet etching)
- Conclusions

Thin Films

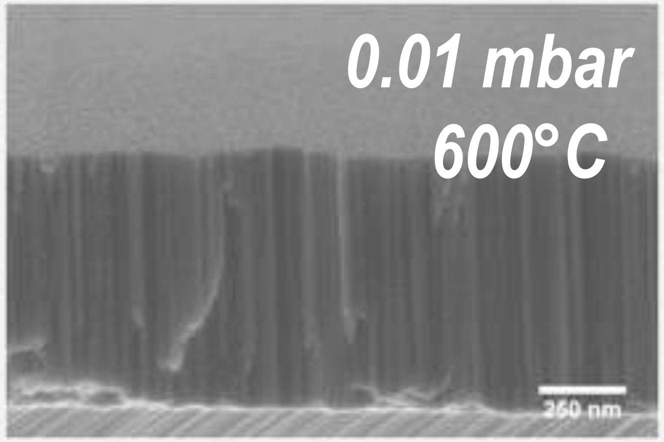
- Thin films are for utilized in many applications as active components, but they are also often perfect model systems to study fundamental aspects of the materials, their properties, and functionality.
- For applications the "cheapest" deposition methods will be applied, but for fundamental studies the most "flexible" method with the highest control is often used.
- For achieving a high control over the films a understanding of all processes are required, i.e. from the deposition method to the film growth.

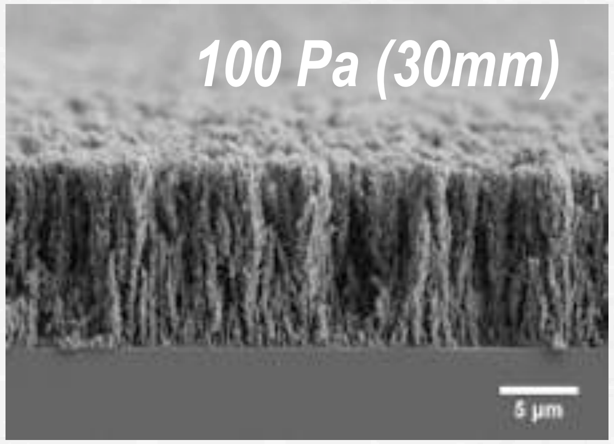
Why laser "printing/ deposition for thin films? or structuring by laser?

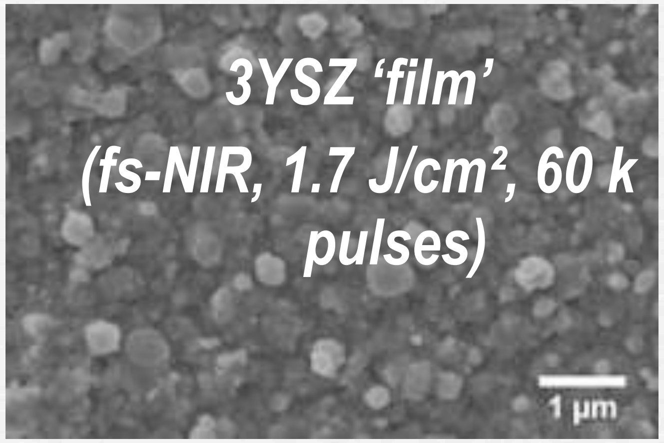
- Thin films of almost any material, "solvent" and nozzle free, resolution, speed, and quality.
- Structuring of any material (see talks before)

Thin films as model systems

- Possible to create well defined surfaces and materials on inert substrates
- Possible to vary crystallinity and orientation
- Possible to vary composition fast (e.g. out of ABO_3 + $A'BO_3$ all compositions of $A_{1-x}A'_xBO_3$)
- Possible to obtain phases which are difficult to obtain with other methods.
- Dense to porous films (even micro- to nano-particles are possible)


0.01 mbar
600°C
250 nm


100 Pa (30mm)
5 µm


3YSZ 'film'
(fs-NIR, 1.7 J/cm², 60 k pulses)
1 µm

Pulsed Laser Deposition

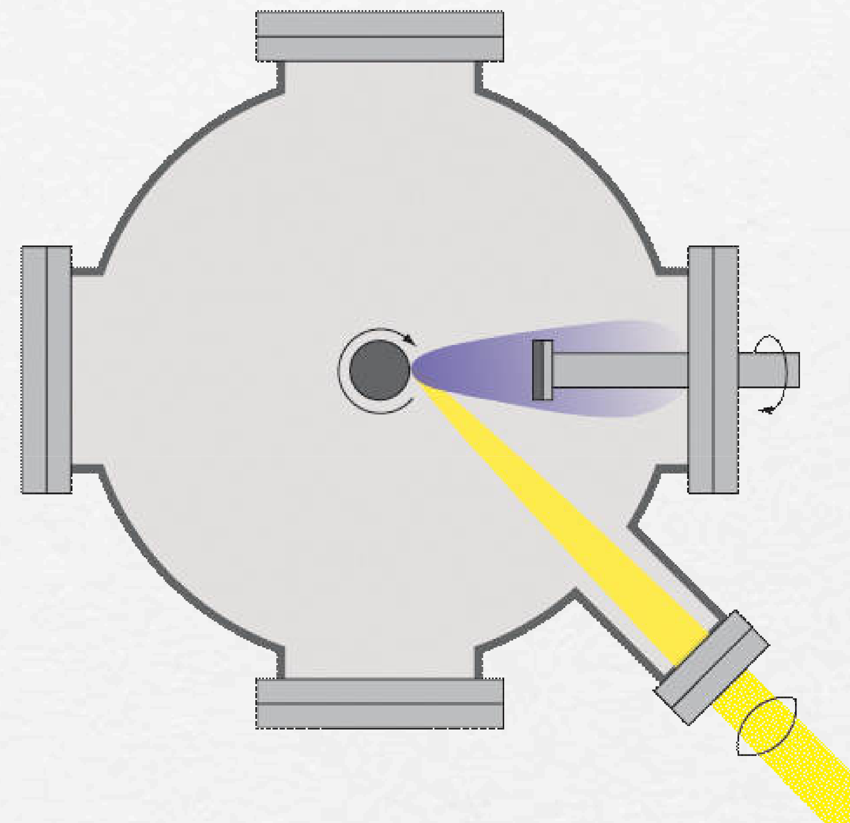
- ☐ Oldest method: first report in 1965, but "hot topic" from 1987 (high T_c films).
- ☐ High power laser interacts with material, resulting in laser ablation
- ☐ Formation and expansion of a plasma
- ☐ Deposition of material of plasma onto a substrate, resulting in thin film growth

⇨ Perfect method for inorganic materials/complex oxides

PLD: setup

PLD specific hardware: conceptually very easy:

- Laser: most often pulsed UV laser (excimer). Advantage: external energy source, extreme clean process.
- Optical elements: mirror, lenses, optional: homogenizer
- HV to UHV chamber with pumping system (most common: turbo pumps)
- Rotational and translational movement of targets (computer controlled)
- Heating system for the substrate: resistivity, laser or lamp.
- Variable target to substrate distance.
- Deposition in both inert and reactive background gases.
- Deposition rates ~100 Å/min, thickness control in real time by turning the laser on and off.



Typical deposition parameters:

- Fluence = 0.1 - 10 J/cm^2
- Targets: mainly discs or rods
- Distance target-substrate = 3- 8 cm
- Substrate temperature: RT - 900°C
- Pressure: UHV to ambient pressure.

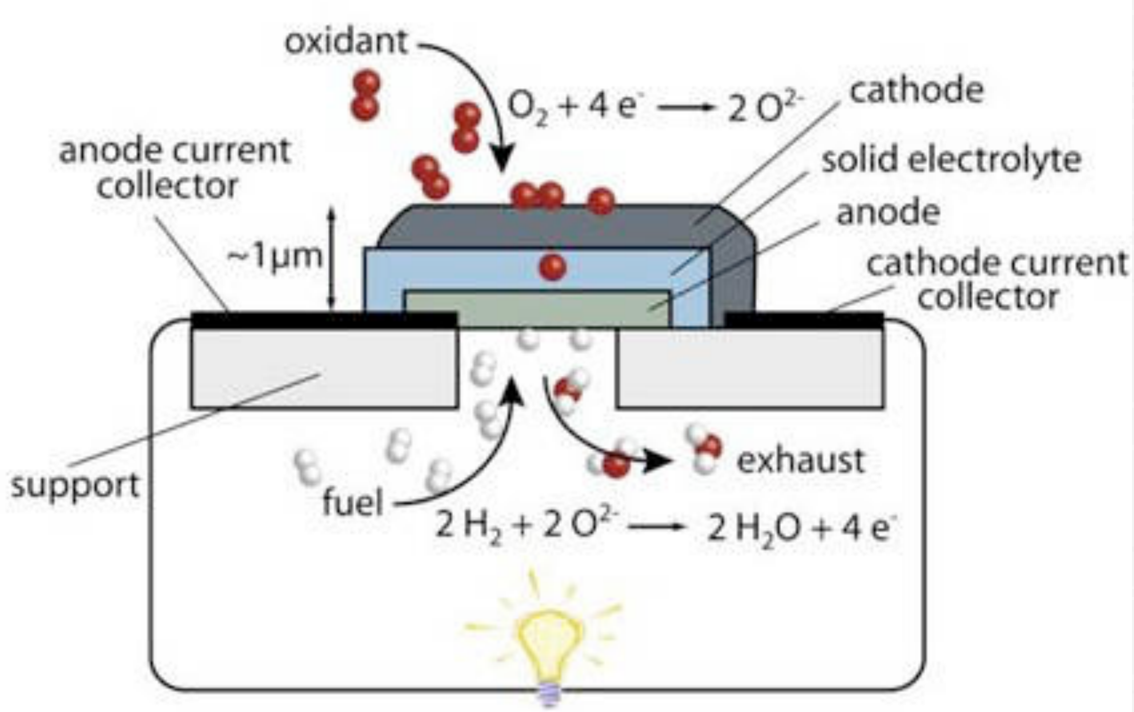
in collaboration with:
L. Gauckler and group
ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

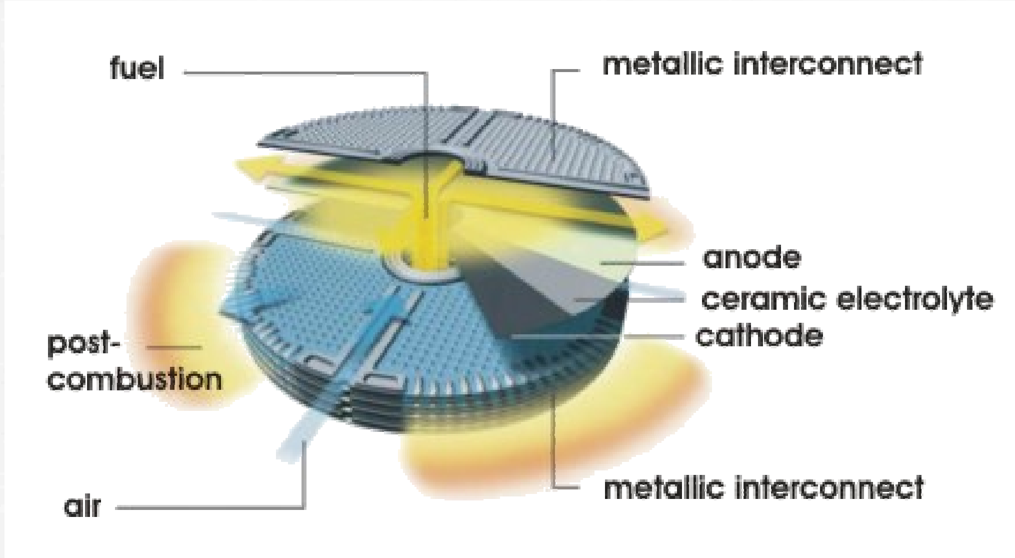
Ion Conductors, i.e. YSZ,

for micro Solid Oxide Fuel Cells (μ-SOFC) as model system but also as test for best deposition method

Solid oxide fuel cell (SOFC)

- direct electrochemical conversion
- chemical energy → electrical energy

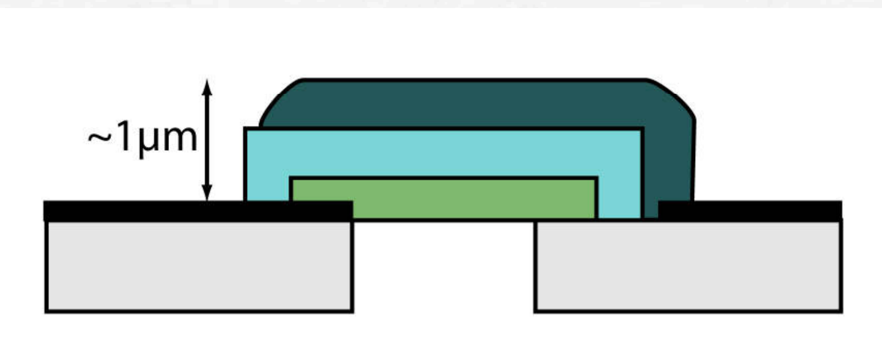




$T_{operation}$: 800-1000°C

- dense, gas tight electrolyte
- porous electrodes

Micro-SOFC



Conventional SOFC:

- d of several hundred µm

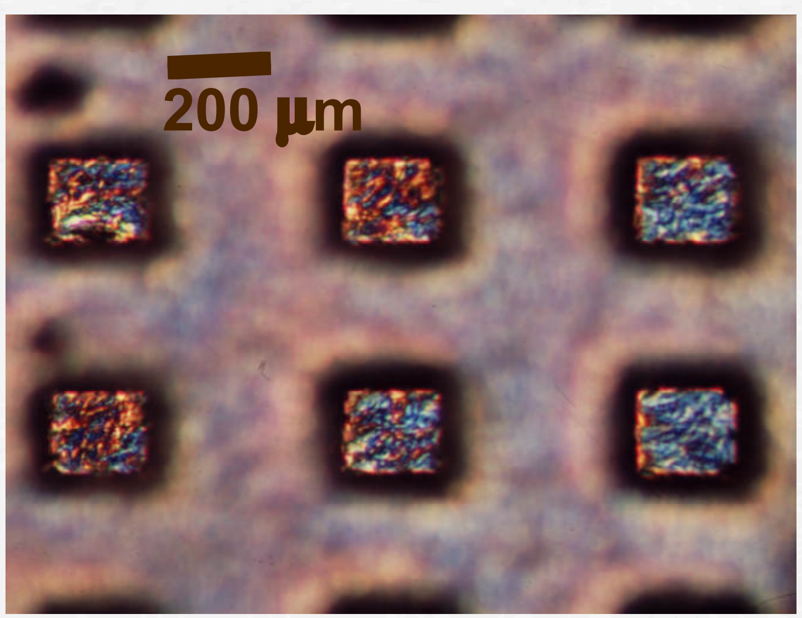
Thin film technology

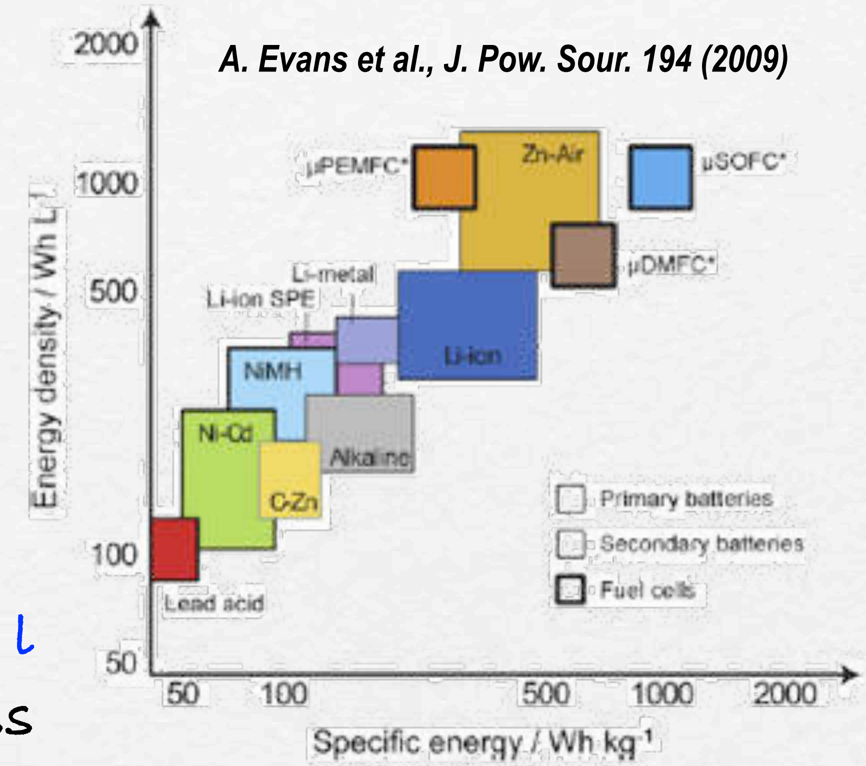
- enhanced performance
- reduced operational temperature results in less degradation

Aim:

- 400 mW cm^{-2} at 500 °C

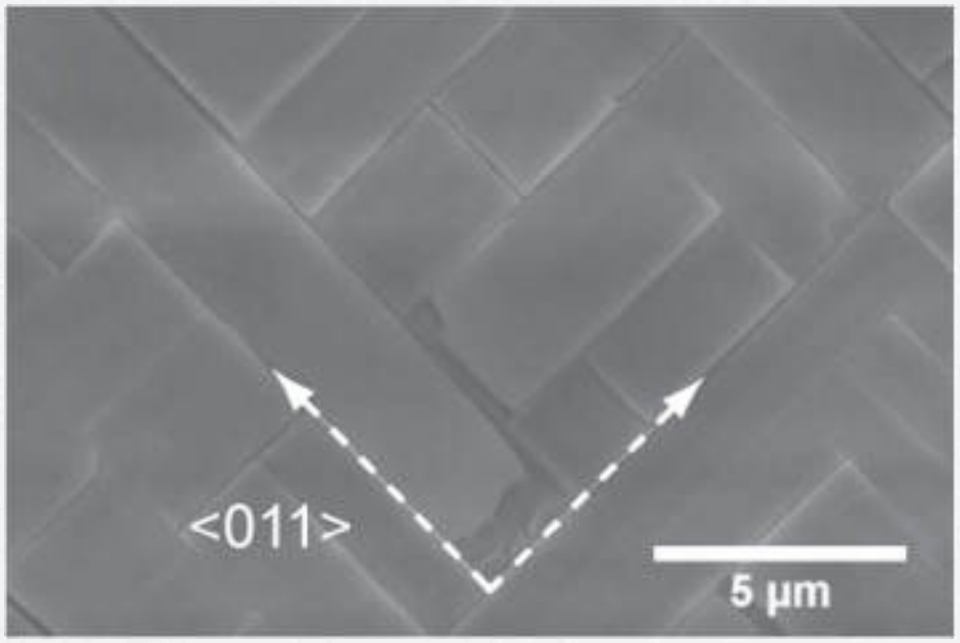
- optimization of the materials
- novel cathode materials





e20_Adaptive Materials

ns-Laser Ablation of fully stabilized YSZ (+8 mol% Y_2O_3)

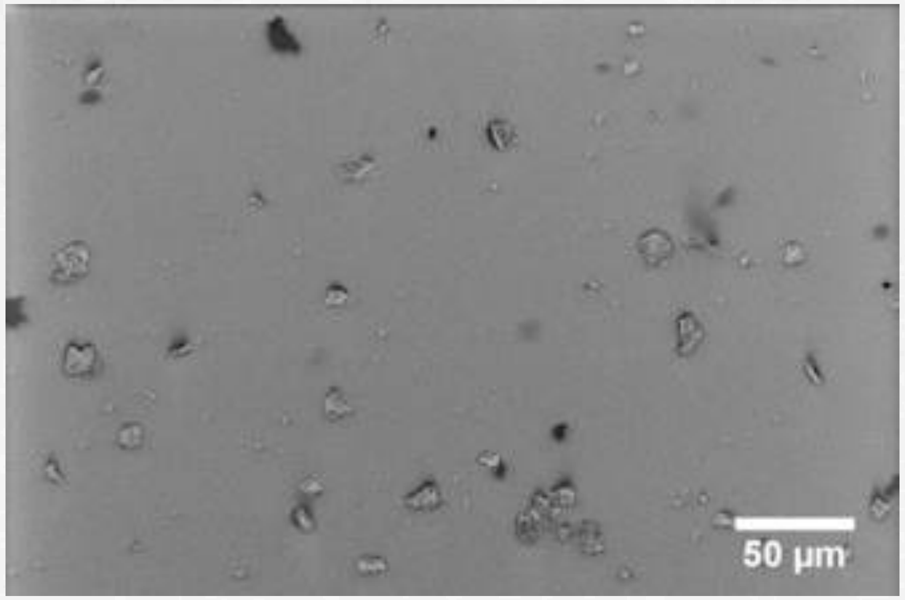


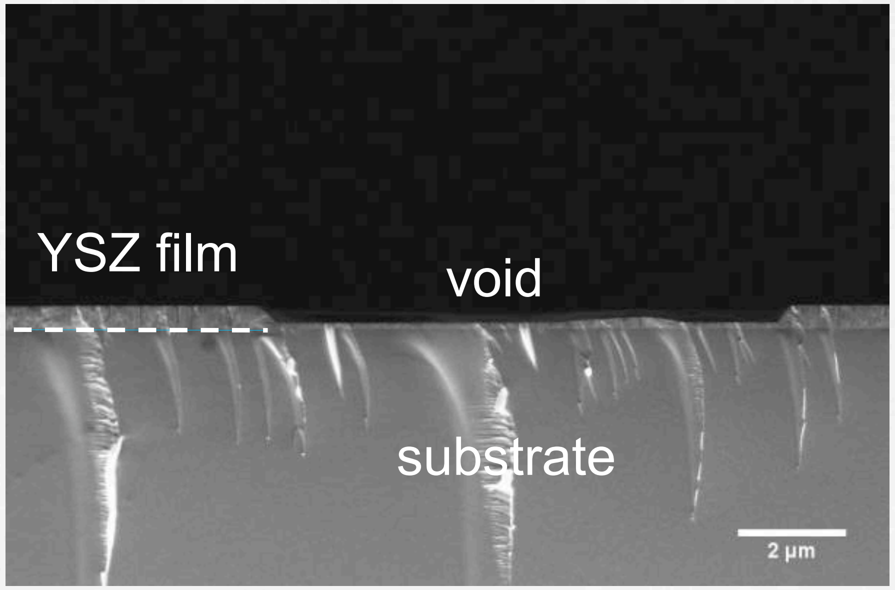
- Ejection of µm-sized fragments on the µs-ms time scale, v_{max}: 350 km/h

Shadowgraphs
9.5YSZ (ArF, 4.0 J/cm²)

- Extensive laser-induced formation of surface cracks on the target
- Particles on surface of the films and voids in the film

8YSZ films (KrF, 4.0 J/cm², 36k pulses)





S. Heiroth et al. J. Appl. Phys. **107**, 014908 (2010).

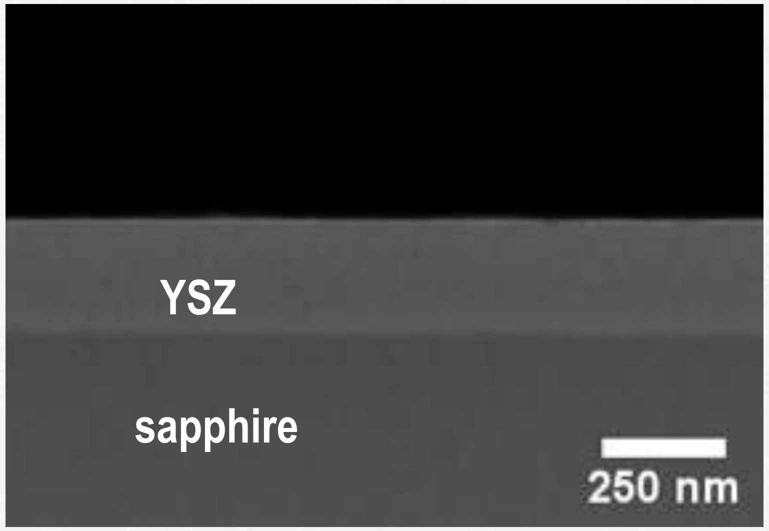
Problem: Particles for 8YSZ

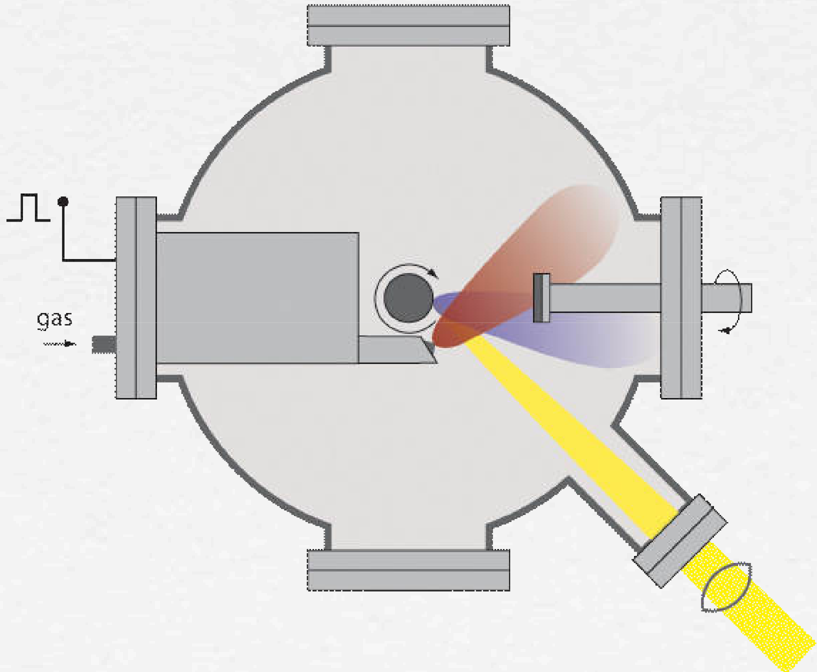
The particles are due to the structure and properties of 8YSZ. It may therefore be impossible to avoid them completely (we tested wavelengths, pulse lengths, sintered polycrystalline vs. single crystal, pressure etc.)

Two possible solutions: modification of PLD or different YSZ, e.g. 3YSZ.

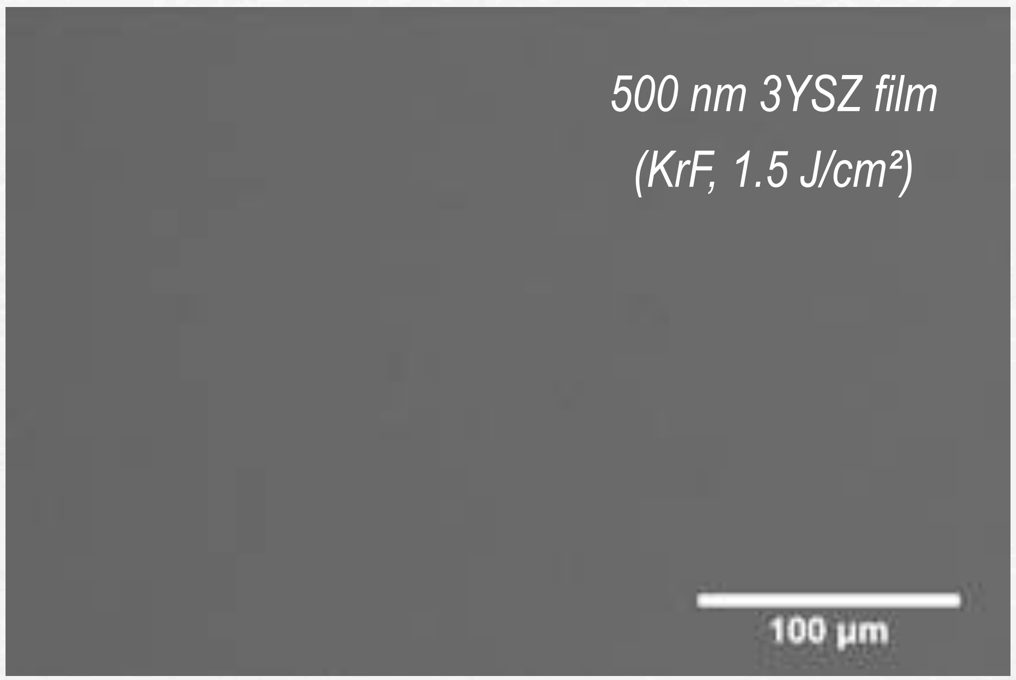
- Prevention of particle transfer to film possible by PLD modifications:

  Example: Crossed synchronized supersonic gas pulse (N_2O)



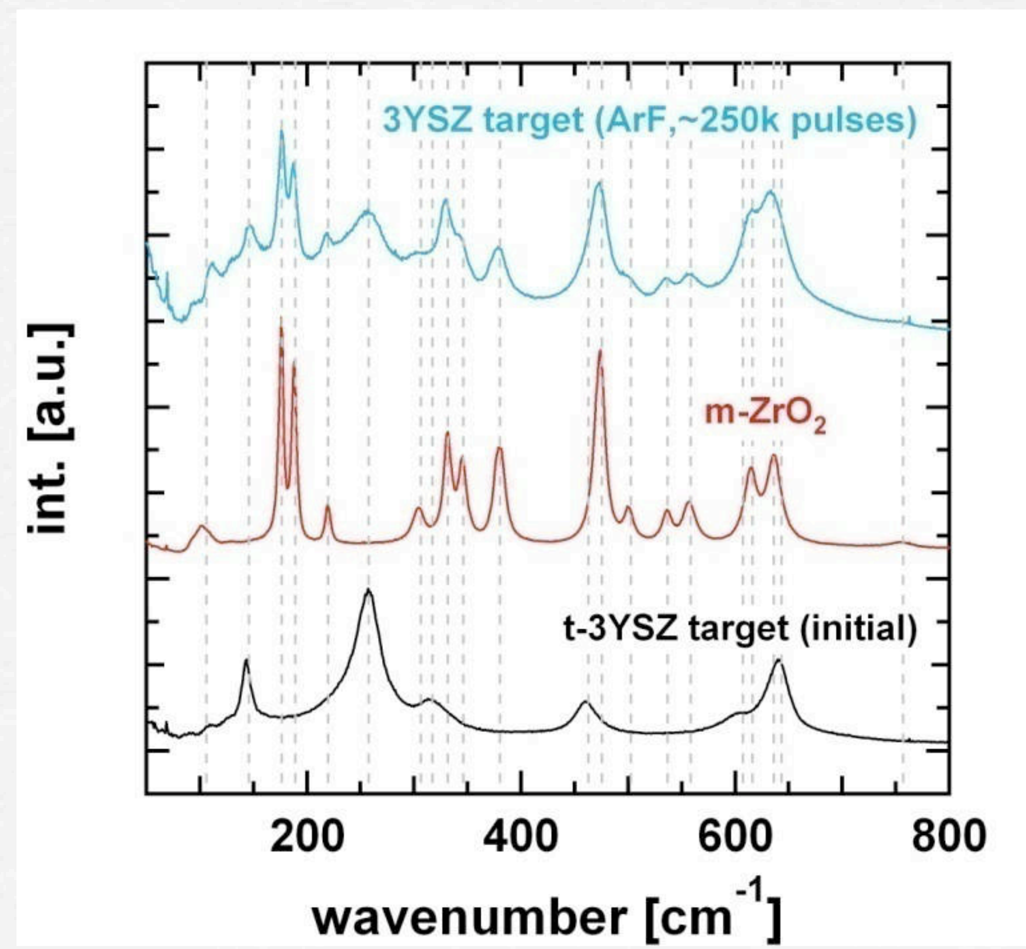


ns-Laser Ablation of partially stabilized YSZ (3mol% Y_2O_3)

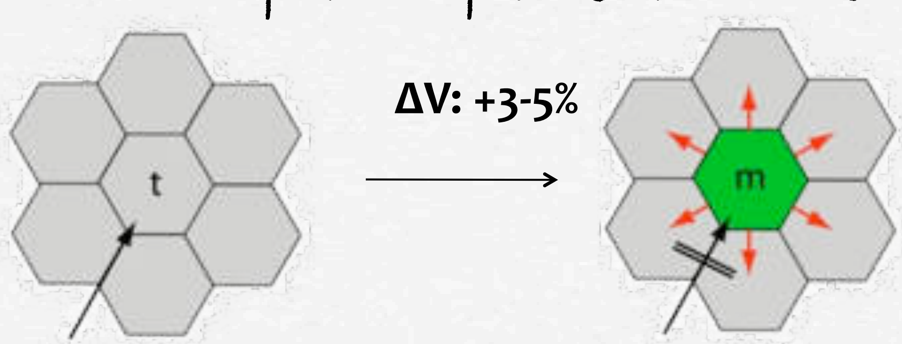


Shadowgraphs
3YSZ (ArF, 4.0 J/cm²)

- No fragmentation ➡ Particle-free films



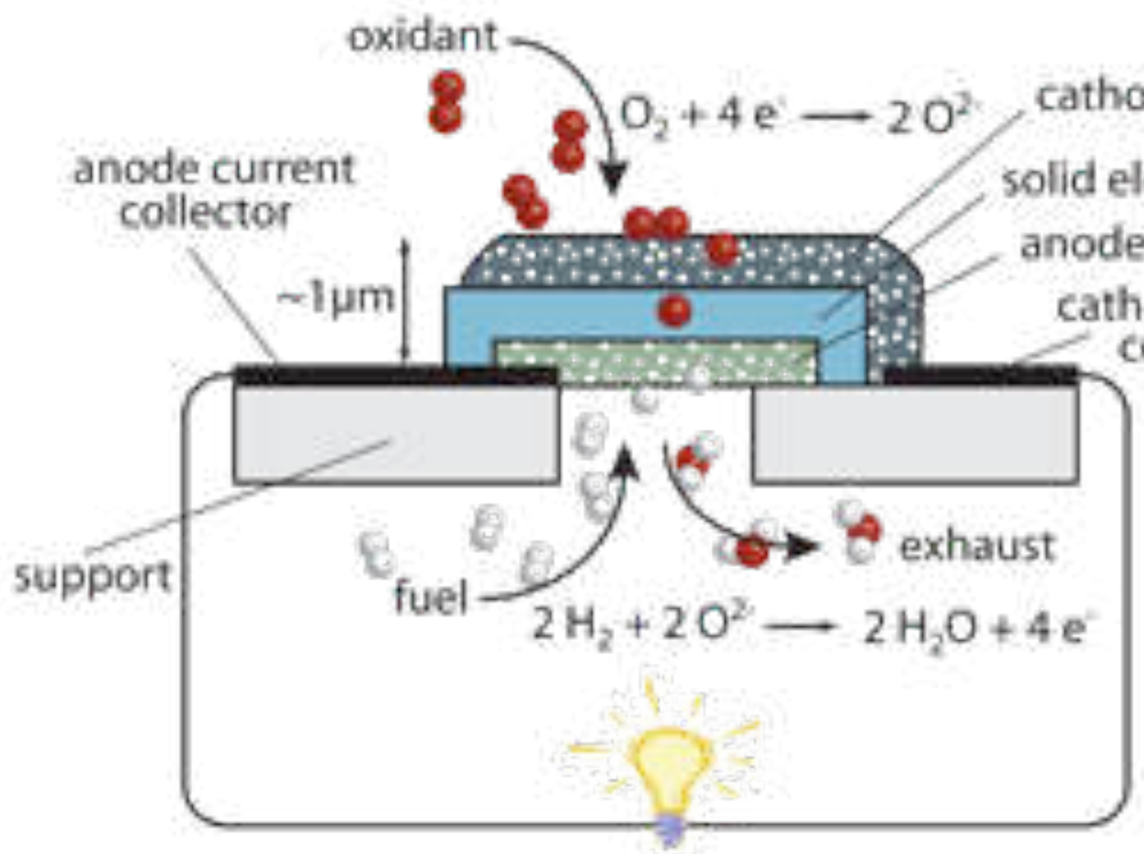
- Enhanced fracture toughness by laser-induced partial phase transition:



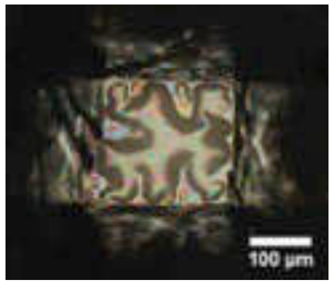
Stress-field generated around transforming grains counteracts crack propagation

in collaboration with:
L. Gauckler and group
ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Low temperatures extreme important to minimize strain on freestanding thin layers



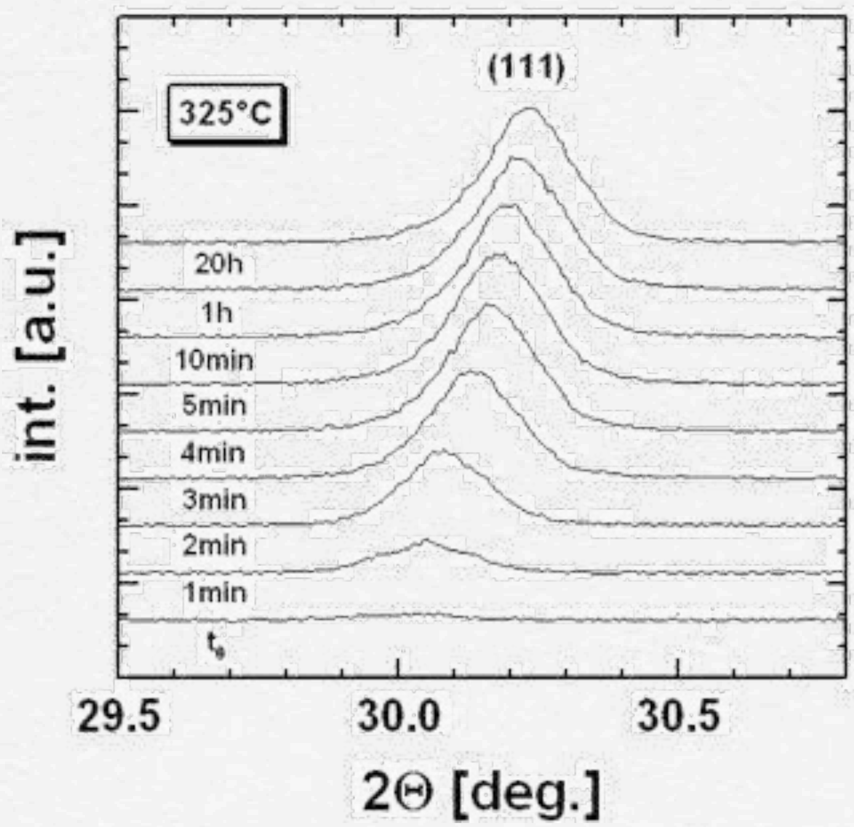
~ 700 nm thin
8YSZ membrane



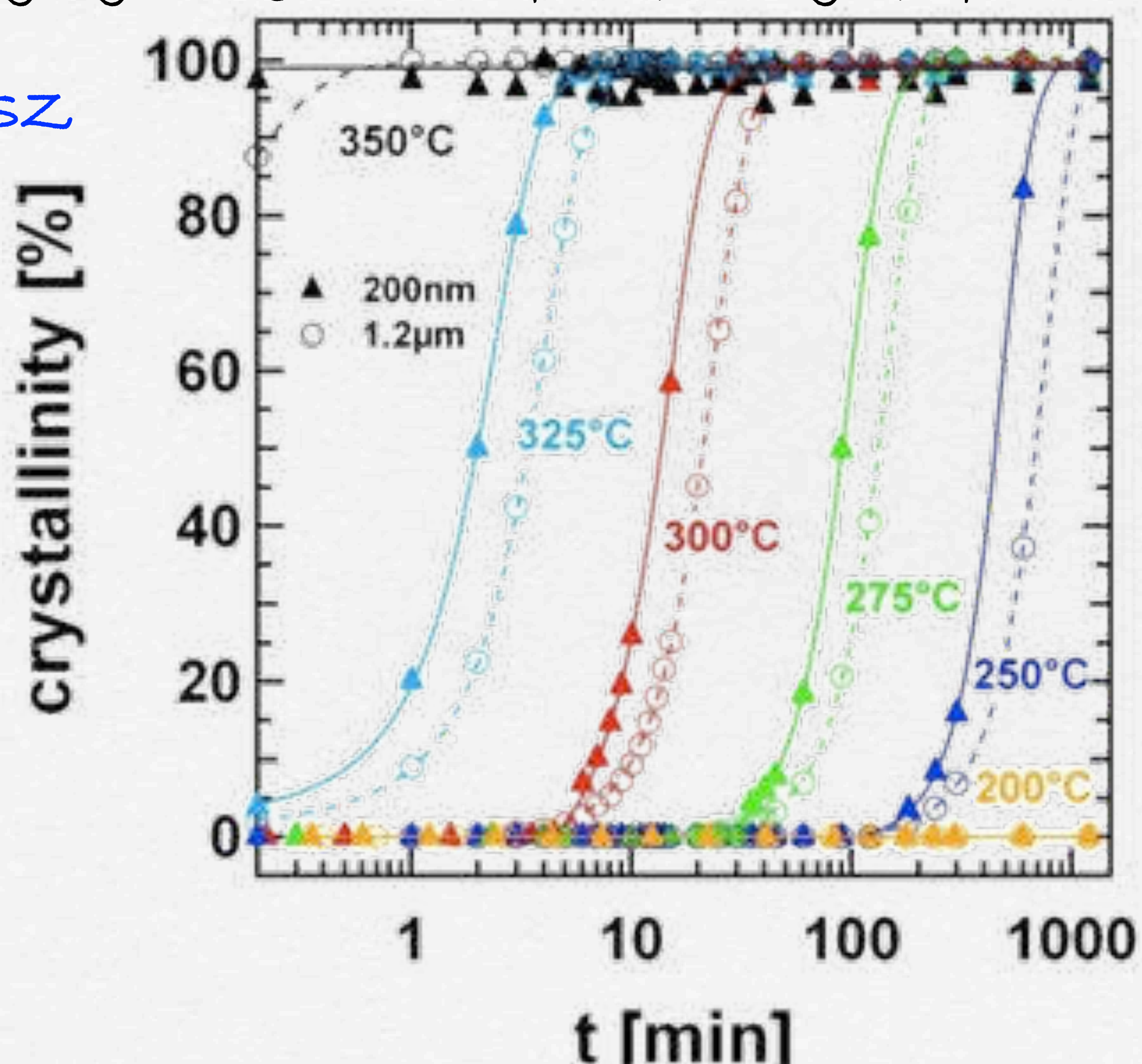
Crystallization of amorphous 3 and 8YSZ layers by annealing

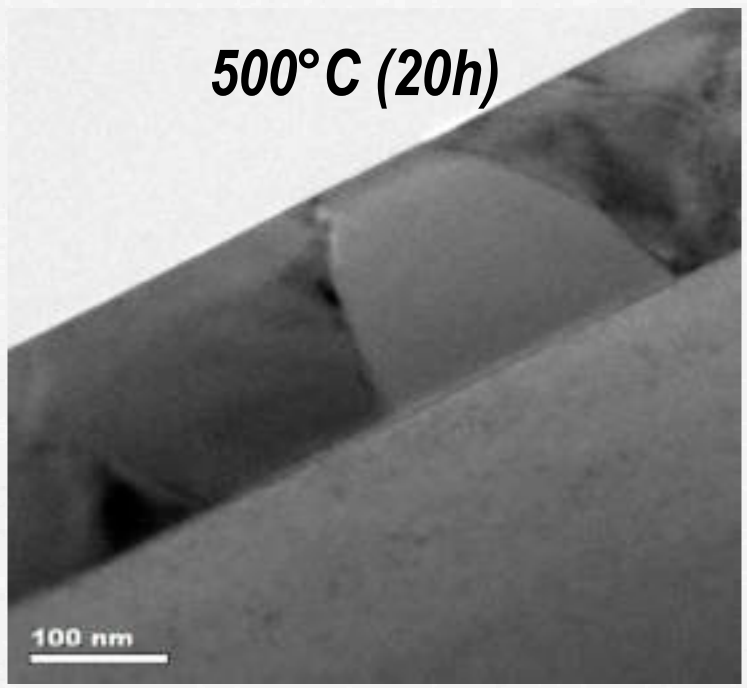
- Crystallization of a-8YSZ PLD layers requires low thermal activation ($T_{cryst.}$: ~230°C)

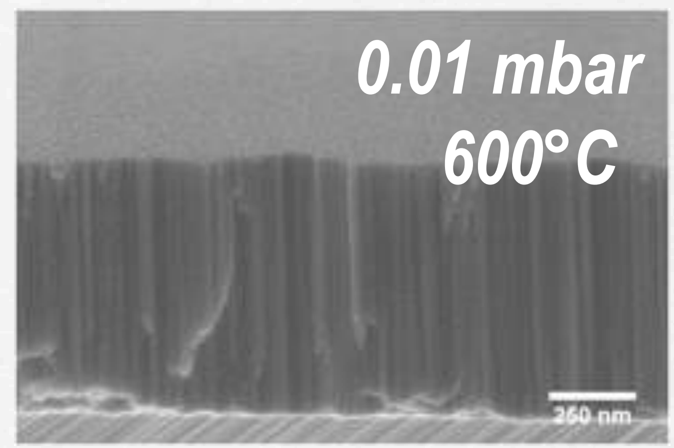
Comparison: $T_{cryst.}$: ~400°C (a-8YSZ films by spray pyrolysis), >900°C (a-8YSZ films by r.f. sputtering)



both for 8YSZ

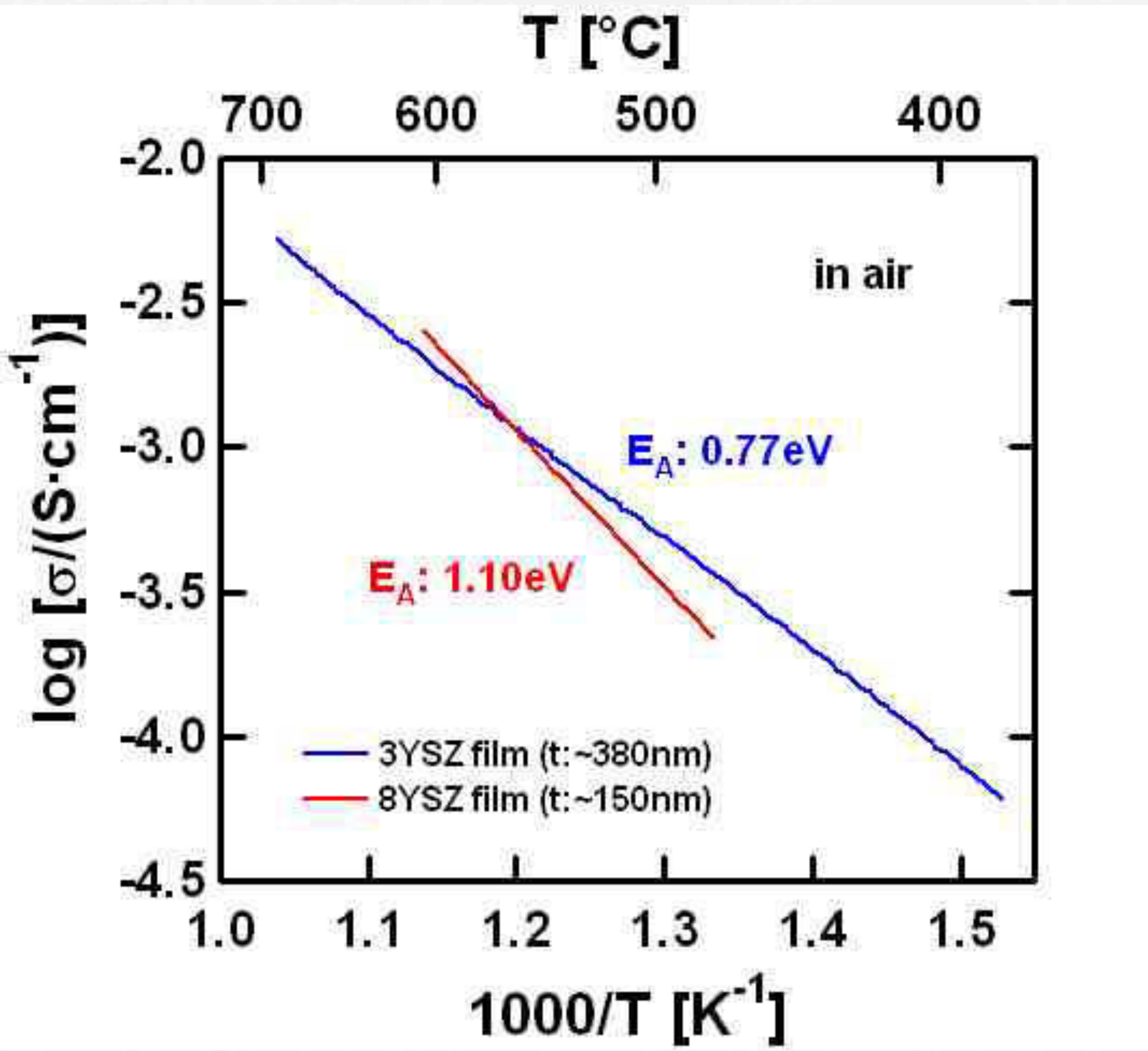






- Large grains (dimensions: ~250 nm for 8YSz [3YSZ=3-4 times larger], no texture)

In-plane conductivity



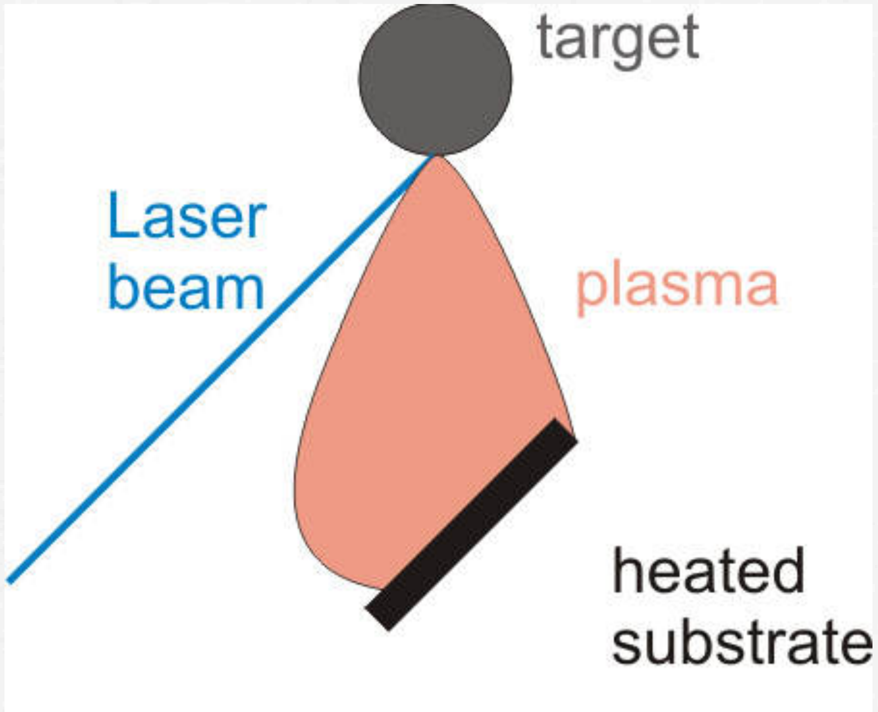
3YSZ films:

- **σ** higher or comparable to the state of art material, i.e. 8YSZ, at low T (up to ~550°C = T-range of micro-SOFC)
- particle-free YSZ films can be obtained at moderate fluences

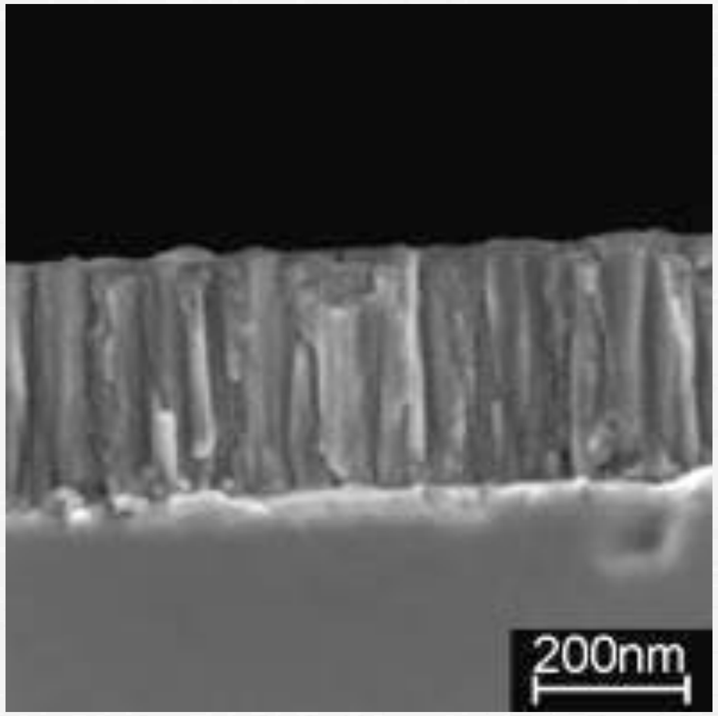
3YSZ eligible thin film electrolyte in LT-SOFC

New Approach: Tilted PLD

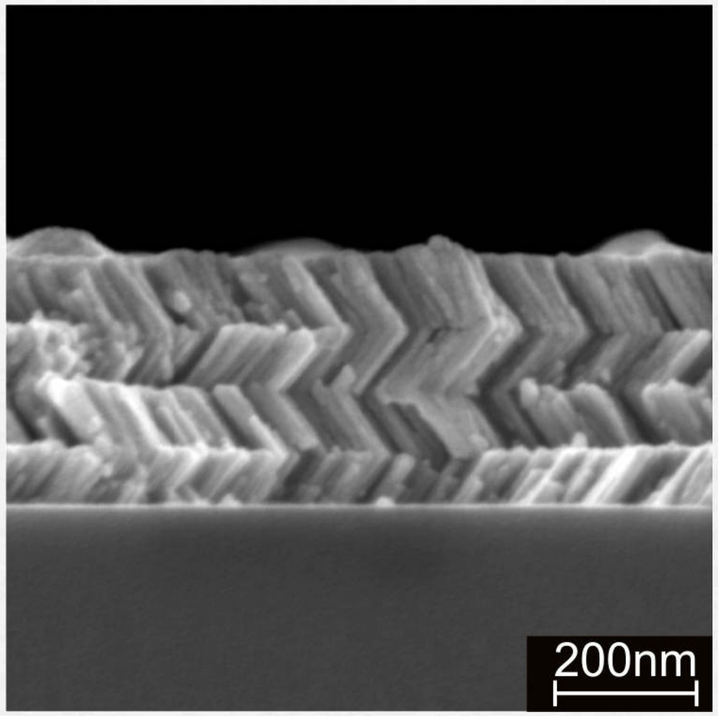
PLD setup for tilted growth



conventional PLD



zigzag structure



- Standard PLD with plasma plume perpendicular to the substrate surface yields a columnar structure.
- With a tilt between plasma plume and the substrate surface a tilted growth of columns is achieved.
- Zigzag structures are obtained by in-plane rotations of the sample during deposition

High Resolution TEM of Kink

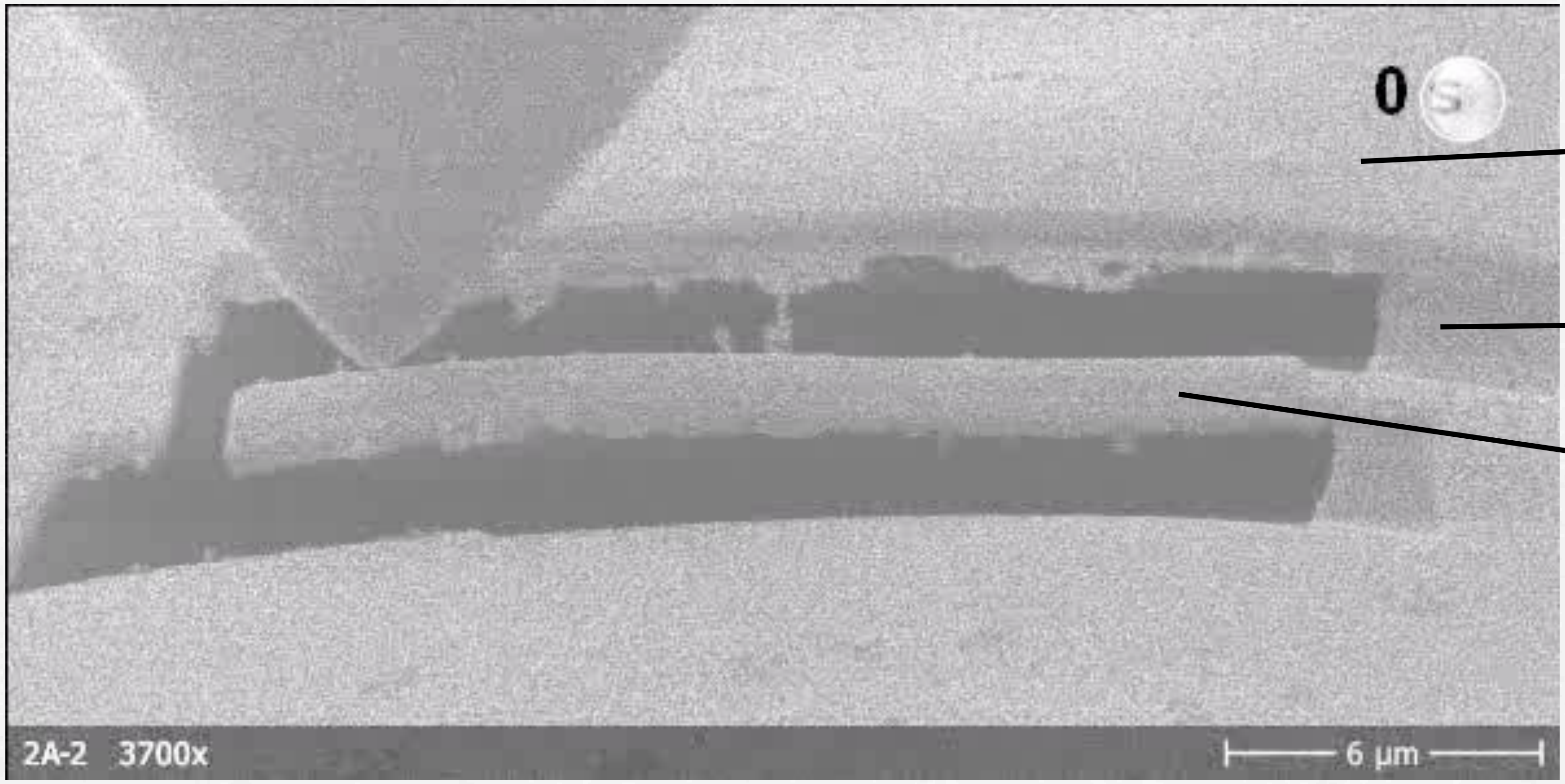
Why zig zag?

- Grain boundaries may be zones to collect impurities which may form a conductive pass (structure different to columnar).
- Defects may be important for conduction (zig zag could have been homo-defects, at the "corners").
- Improved mechanical properties (spring like behavior)

Crystalline growth "around the corner" (no defects there)

(TEM: J. Martynchuk, ETH)

Mechanical Testing



- Beams were cut from free standing membranes with a FIB-SEM (EMEZ, ETHZ).
- Indentation (bending) was observed in-situ by SEM (Empa Thun).
- Strong bending was possible even for a ceramic thin film (e.g. YSZ).
- The load-displacement curve is used to calculate a spring constant from which the materials hardness and elastic modulus are determined.
- More elastic and may be lower activation energy for conduction

What about organic, polymeric or bio-materials?

Organic/Sensitive Materials

- PLD using UV lasers is difficult: decomposition of material
- PLD using resonance mid-infrared PLD can work
- MAPLE: can also work

MAPLE and PLD: shortcomings

- Both techniques require vacuum: expensive!
- Both techniques yield only complete layers with no lateral resolution (or masks are needed).
- Still "problems" with quality and/or decomposition.
- Alternative techniques!

Transfer of layers with lasers

- First papers: Laser Writing (LR) in 1969 and Material Transfer Recording (MTR) in 1970 (R. S. Braudy in Proceedings of IEEE Oct. 1969, p. 1771, and M. Levene et al. in Appl.Optics 9, 2260 (1970). Then Laser Induced Forward Transfer (LIFT), i.e. transfer of Cu, in 1986. (J. Bohandy et al., J. Appl. Phys. 60, 1538 (1986)).
- Also called laser direct write methods (see e.g.: C.B. Arnold, P. Serra, and A. Piqué, MRS Bull. 32, 23 (2007)).
- Advantages: High lateral resolution, defined by laser spot, "solvent-free", highly flexible, multilayer capability, etc.
- Many variations of the original process of have been suggested.

Many Variations

- LMI: Laser molecular implantation
- LITI: Laser induced thermal imaging
- MAPLE-DW: Matrix assisted pulsed laser evaporation: direct write
- LAT: laser ablation transfer
- LIFT (Laser-induced forward transfer) with variation BA-LIFT, DRL-LIFT, ALA-LIFT
- DECAL Transfer

Laser-induced forward transfer

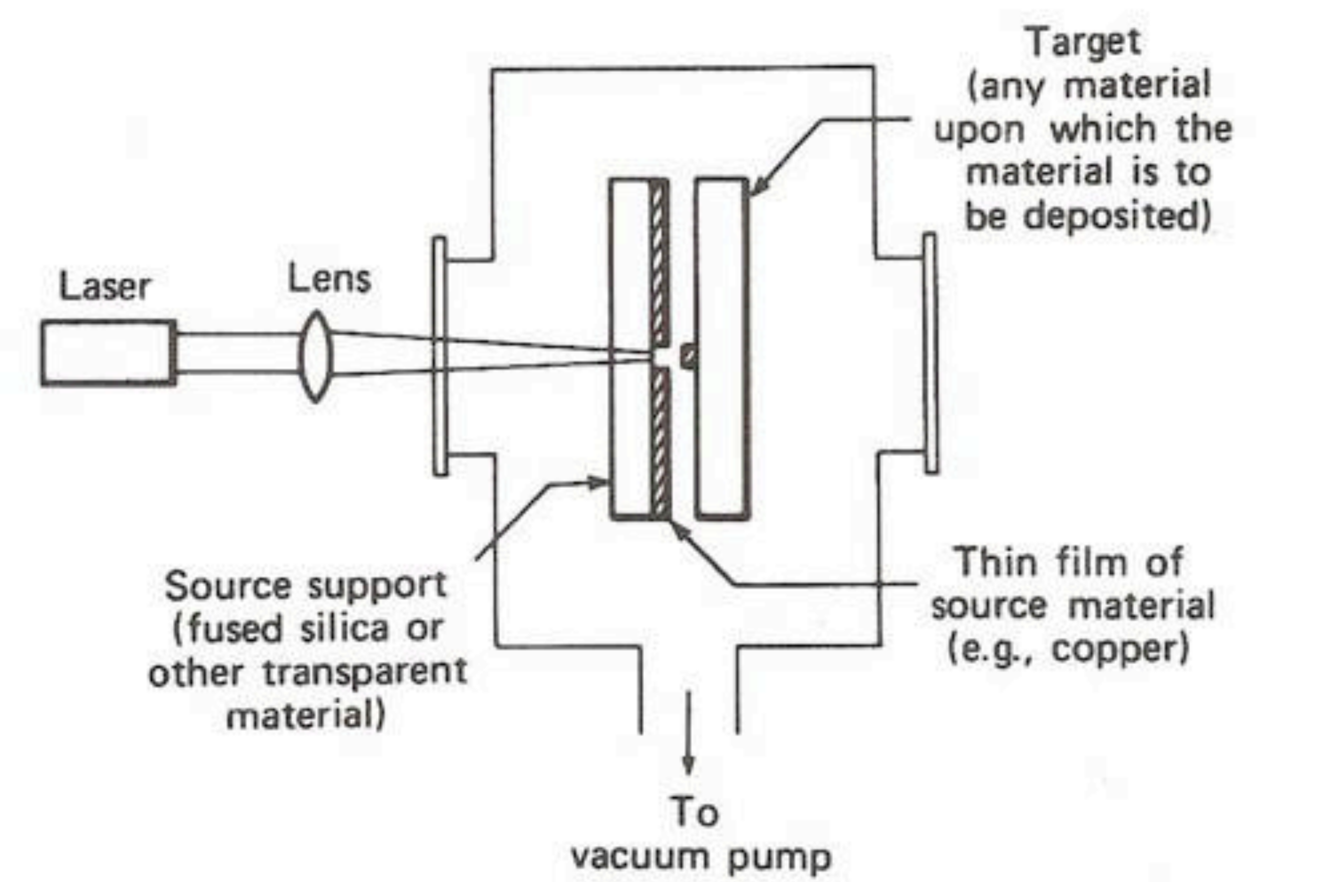
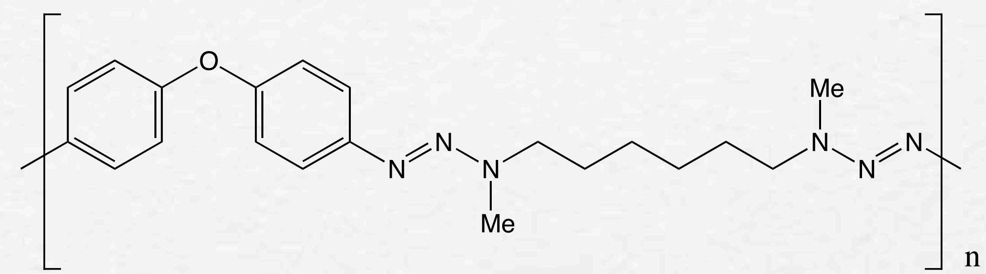


Figure 9.5. A schematic description of the apparatus for metal deposition from a solid-phased precursor. The source material and target are in contact during an actual experiment (from Bohandy *et al.* 1986).

J. Bohandy et al., J. Appl. Phys. 60, 1538 (1986)

Our approach: Development of a variation of LIFT

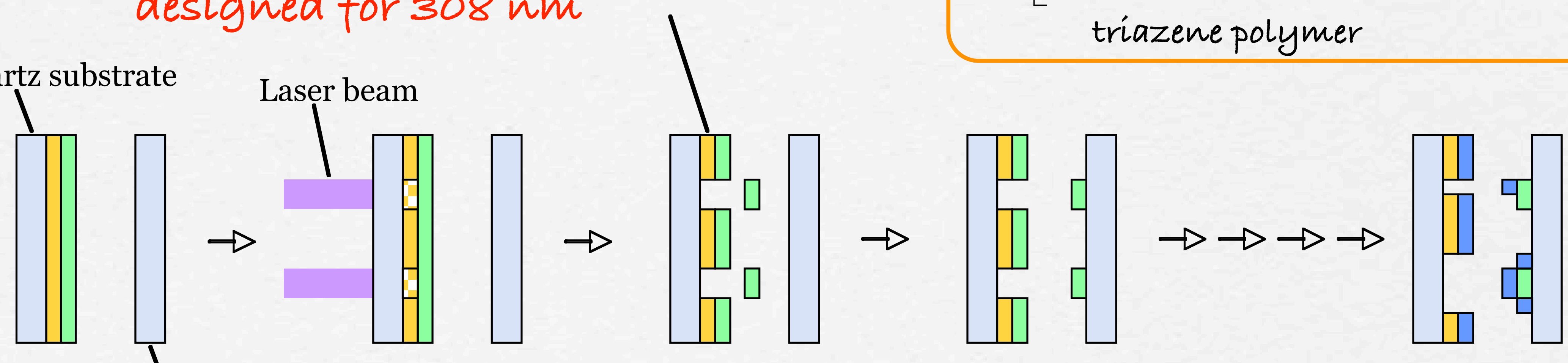
Our approach: Laser-induced forward transfer using a photodynamic release layer



triazene polymer

New approach :

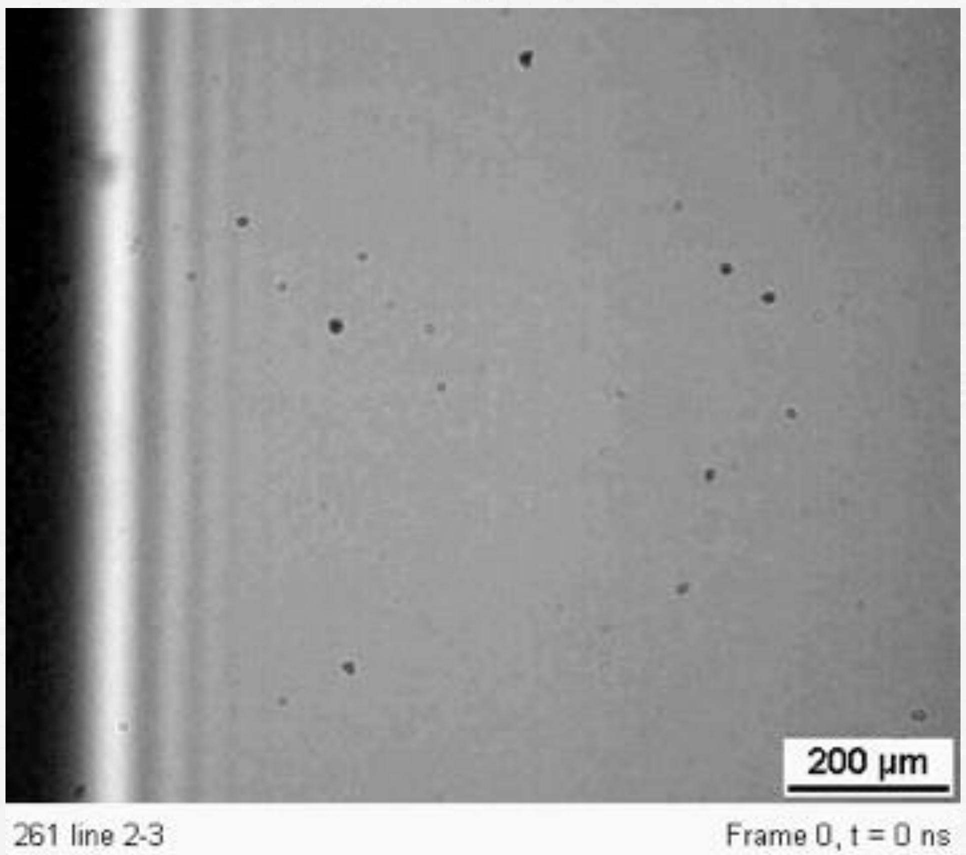
- Use of a UV-sensitive dynamic release layer, designed for 308 nm

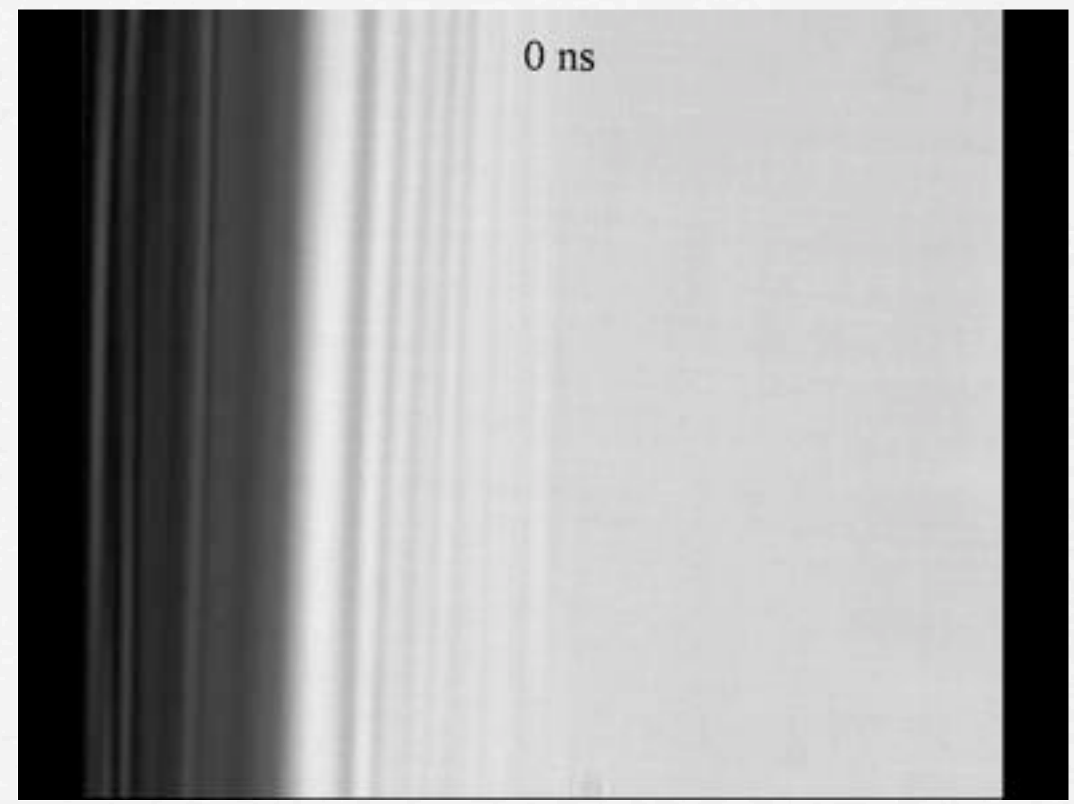


Advantages :

- Dry transfer technique → not limited by the solvent
- Three-dimensional structuring allowed
- Low thermal impact

Printing of solids or liquids





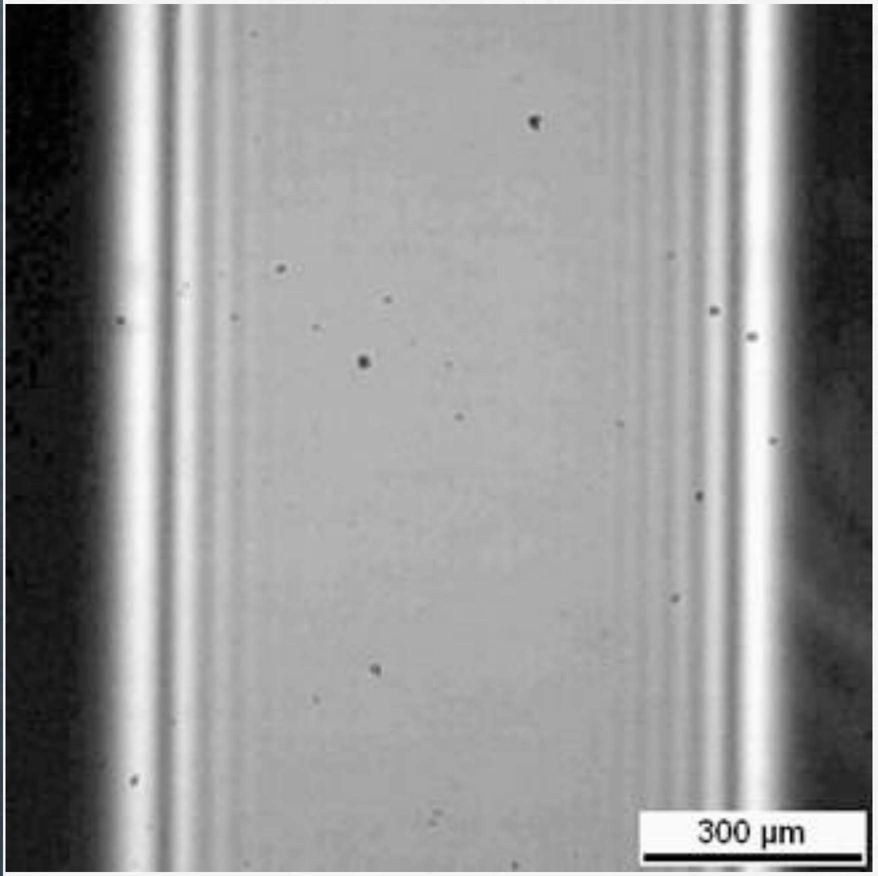
no receiver, triazene 150 nm, Al 80 nm, 270 mJ cm^{-2}

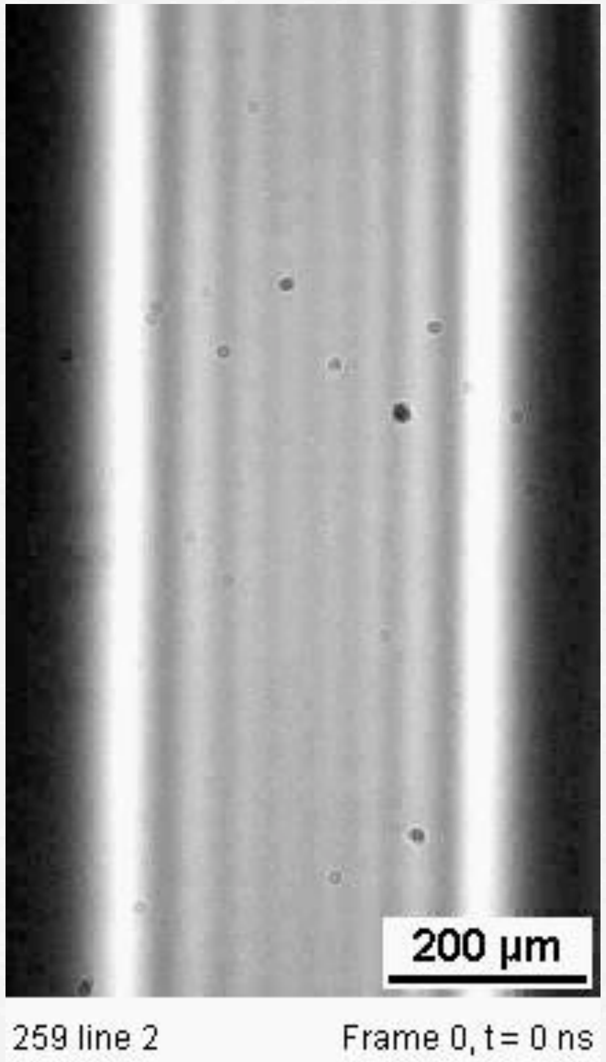
with DRL, 10 micron film and 60 mJ cm^{-2} (193 nm)

40 µm

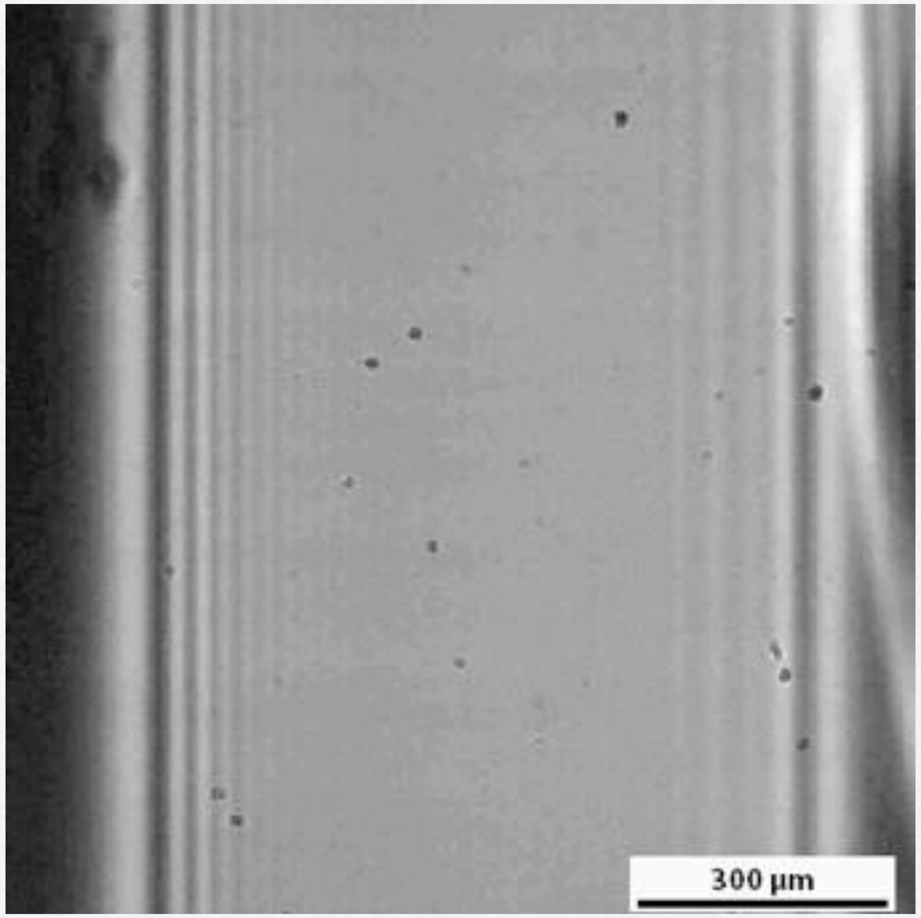
Experiments at various pressures and gaps

at atmospheric pressure: large gap





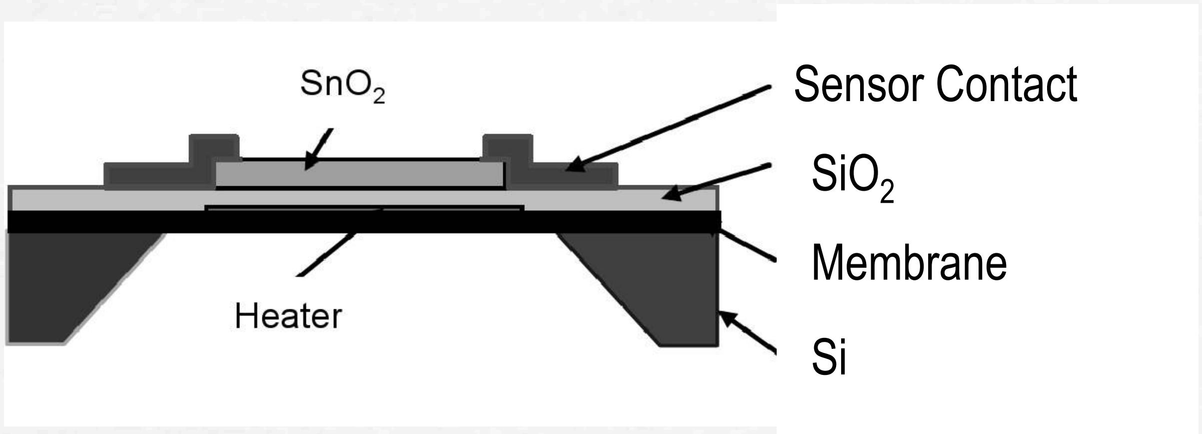
at low pressure (10^{-2} mbar)

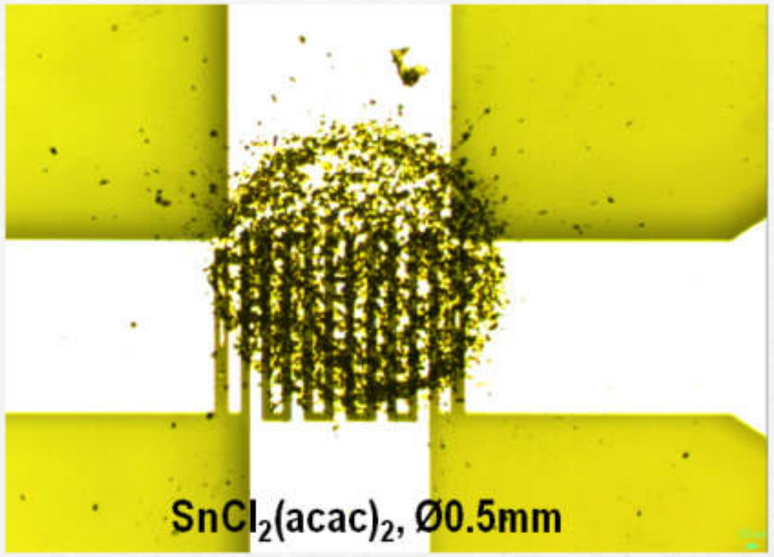


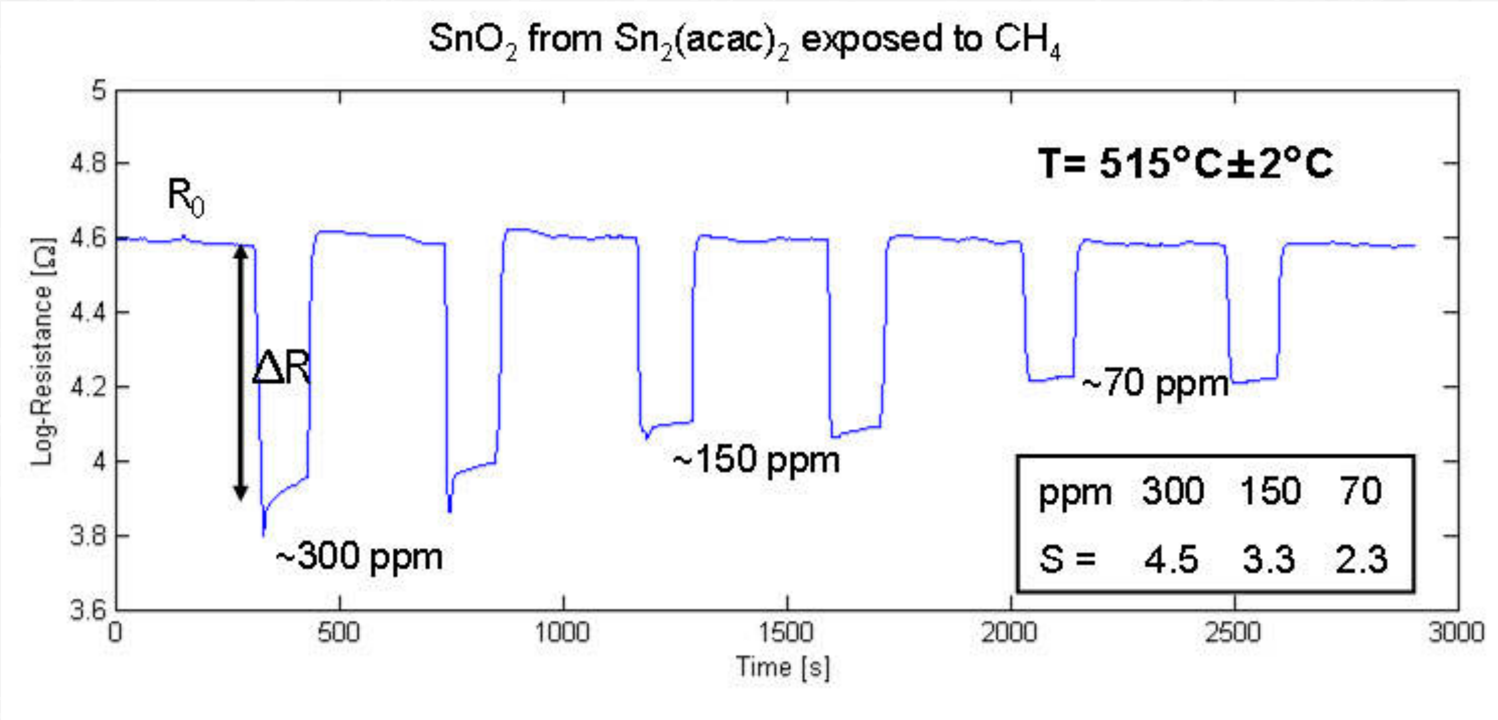
Large distance: flyer falls apart; short distance: shock wave destroys flyer, which never reaches the substrate

No shock wave, but the flyer is destroyed upon impact with the substrate

Gas Sensors based on SnO_2

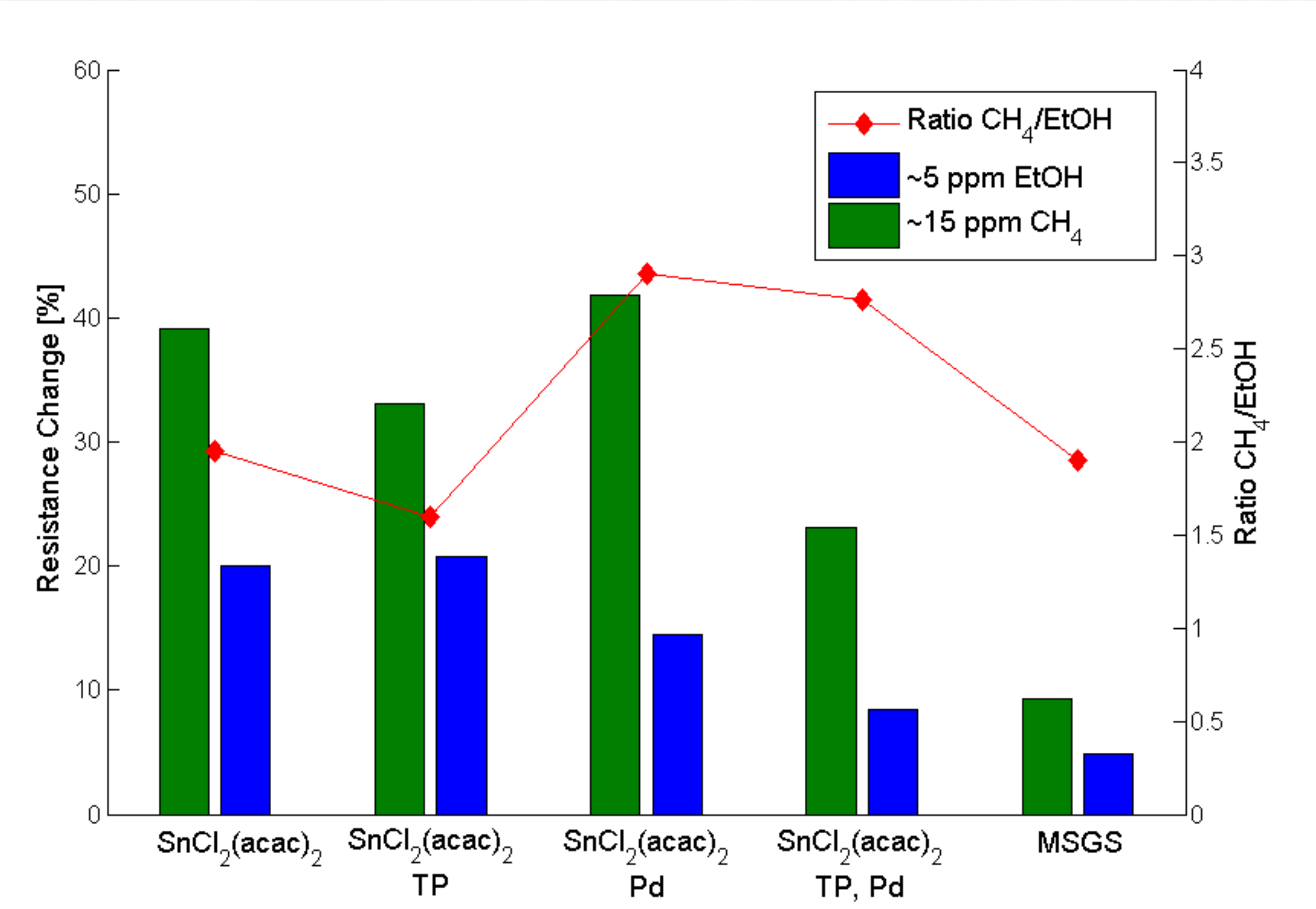






SnO_2 sensors

- New approach: starting material decomposes during LIFT and during thermal annealing after LIFT.



- LIFT printed SnO_2 gas sensors show an up to 4 times better sensitivity towards EtOH (5 ppm) and CH_4 (15 ppm) compared to commercial gas sensors (Microsens Gas Sensors, MSGS), which were printed by inkjet.
- Easy to add co-catalyst to SnO_2 (Pd) using acac-compounds
- Not necessary to develop new ink.

Introduction to organic light-emitting devices (OLEDs)

OLED advantages:

- Thin films
- Electroluminescent, brilliant colors
- No backlighting, large viewing angle
- High quantum efficiencies
- High electrical response times
- Transparent
- Can be deposited from solution (mainly just polymers)
- Emission spectrum can easily be adjusted by chemical synthesis or doping

Sony XEL-1 (11 inch, 3 mm thick display) for ~2500 $

First OTFT driven OLED TV: Sony (May 2010)

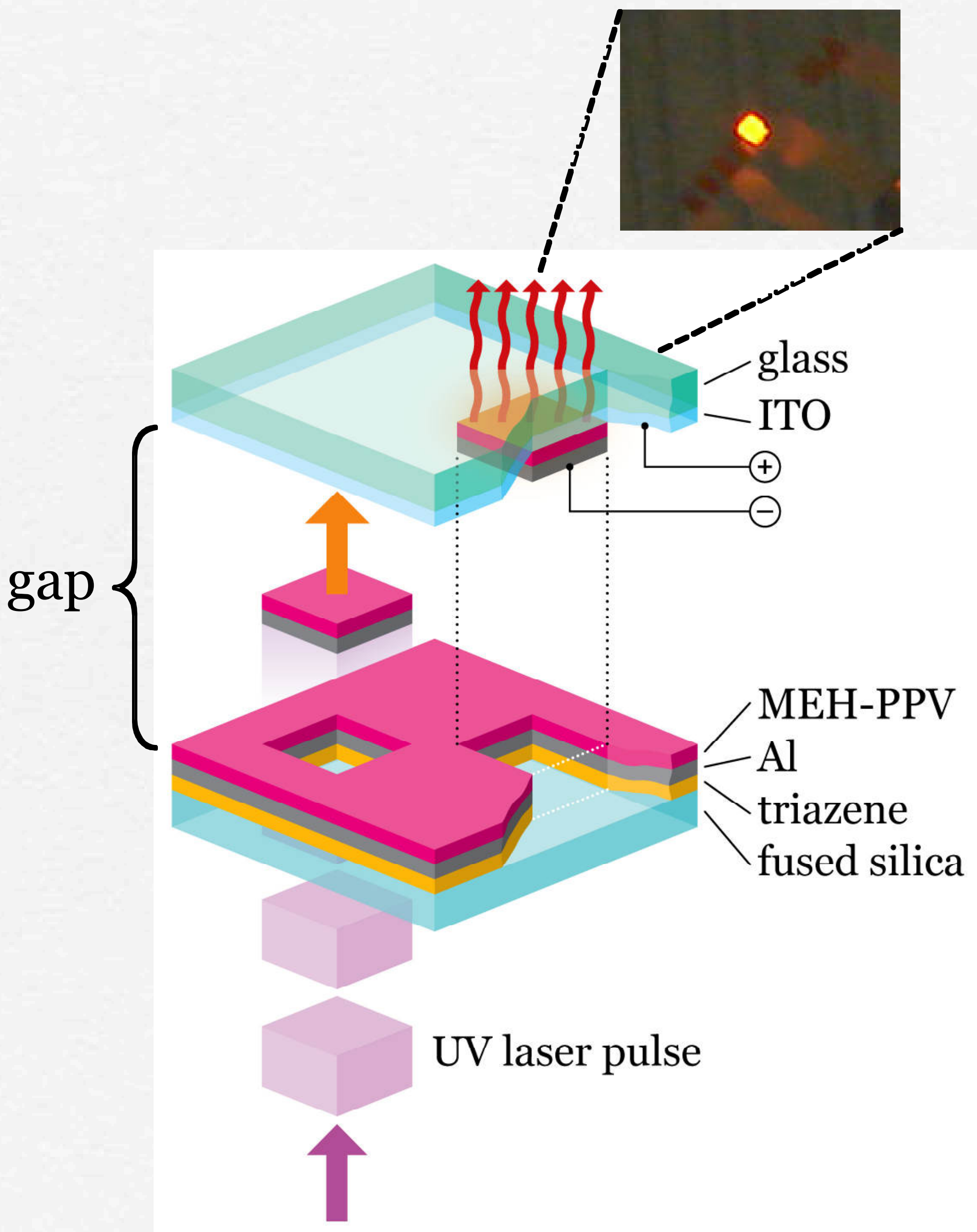
Synaptics concept phone "FUSE" with a 3.7 inch OLED display

August 2009: LG 15" OLED TV available at the moment only in South Korea (~2600$)

Mitsubishi shows 155 inch OLED TV (10*10 cm units, February 2010)

EMPA Materials Science & Technology

Transfer with gap



✓ Transfer works without gap (contact)

But gap better for the process :

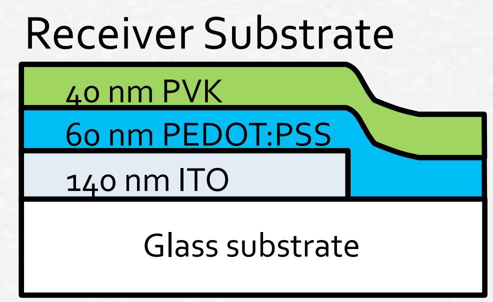
- easier to control
- allows multi-steps deposition

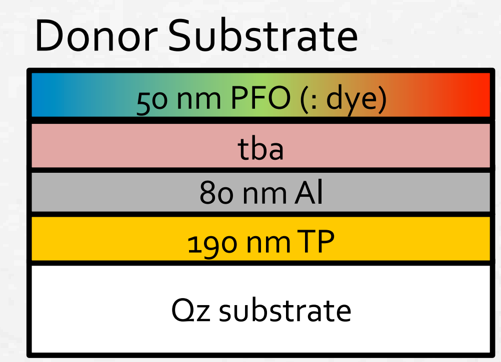
Need to understand the parameters for good transfer with gap

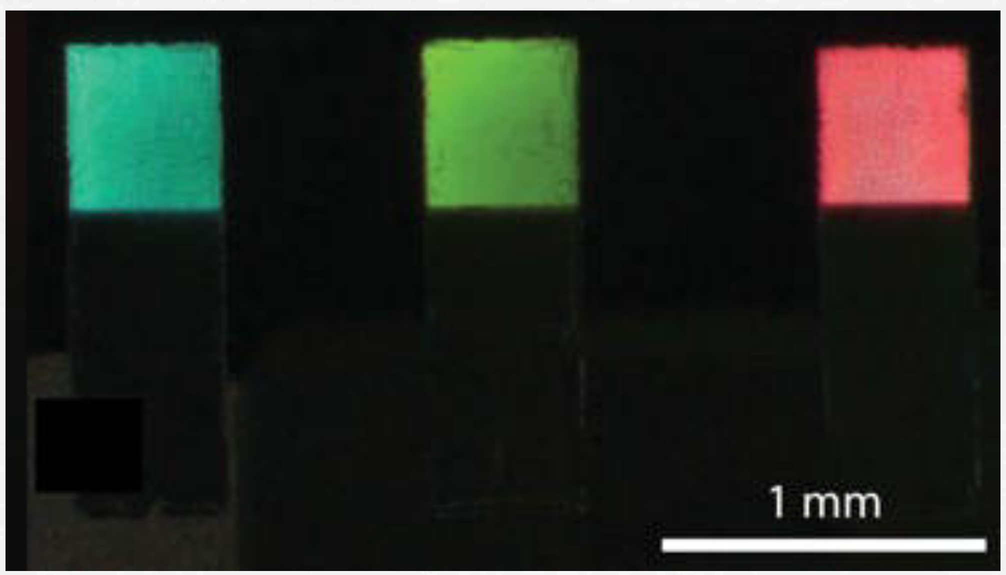
→ time-resolved imaging

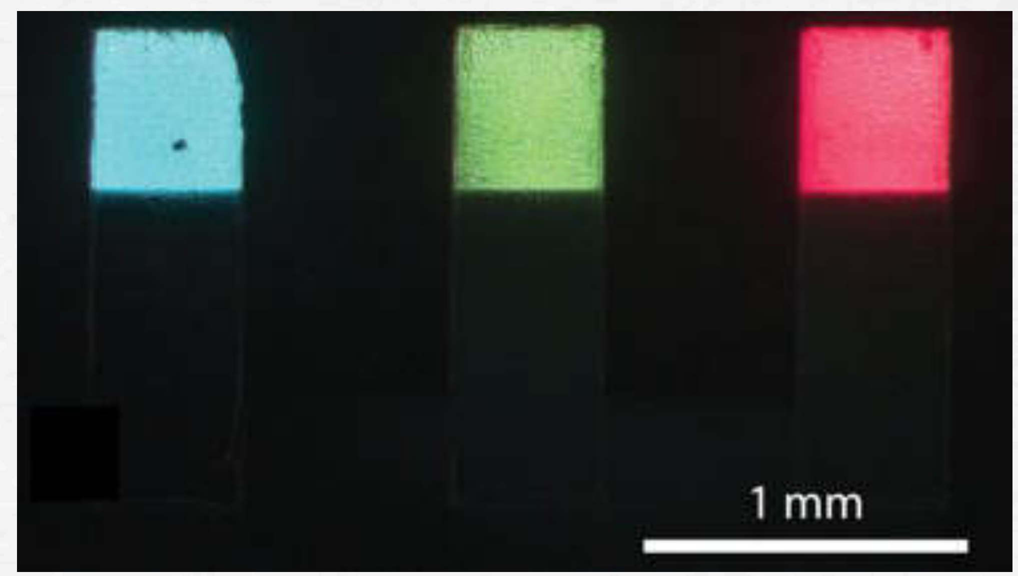
Progress

- Time resolved imaging was used to find condition for transfer with gap a reduced pressure.
- Application and transfer of multilayers
- Transfer of 3 different colors









- Different transfer conditions yield different emission, but efficiency and luminance is similar (slightly lower for green and red, but even higher for blue) than for classical prepared pixels.

LIFT

- LIFT can be used to transfer:
  - Metals (solids and pastes)
  - Cells
  - Proteins
  - Polymers (PLEDs, chemoselective polymers for sensors)
  - Organics (SMOLED)
  - Oxides
  - Semiconductors (NCQDs)
- fully intact with full functionality and high resolution

Transfer through transparent substrate with high lateral resolution is one way to obtain a structure. The other approach is direct structuring, here for transparent materials on the backside (thin films would correspond to LIFT without "collecting" the removed material)

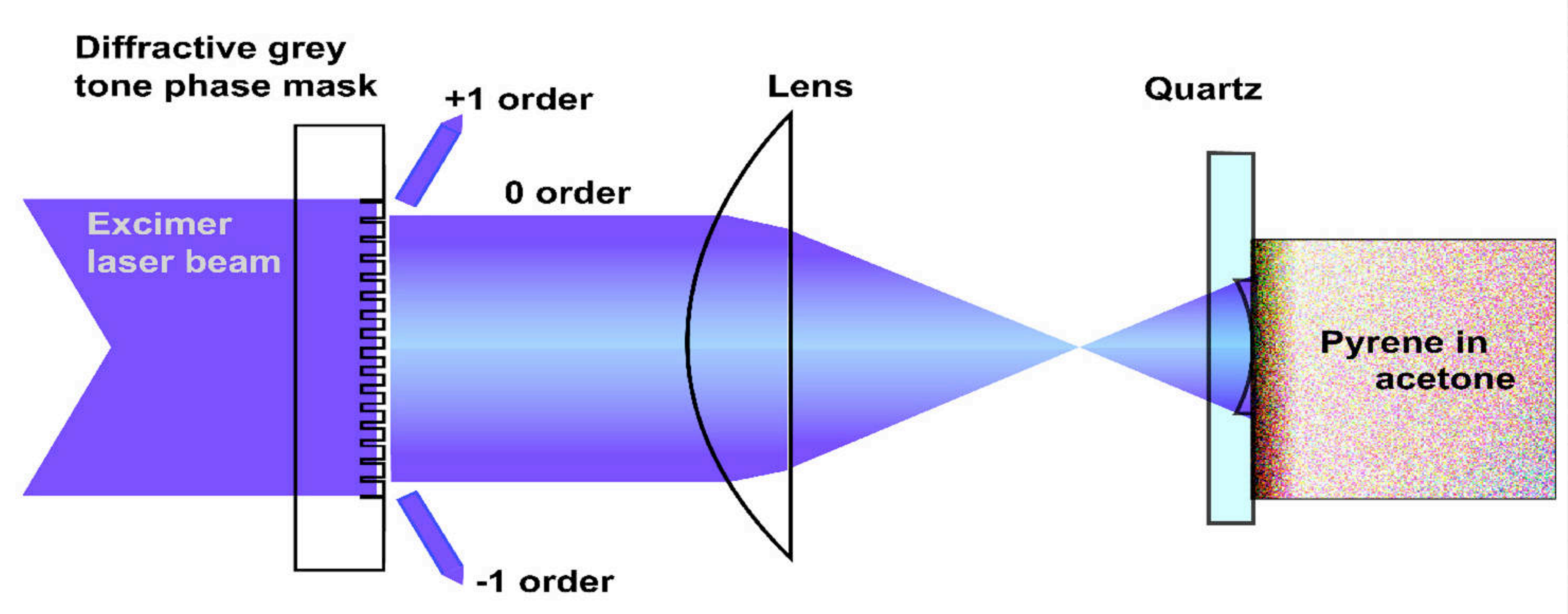
Direct Structuring of Band Gap Materials

Band-Gap Materials: important materials for optics, e.g. SiO_2, CaF_2, BaF_2 etc., but this brings up the question:

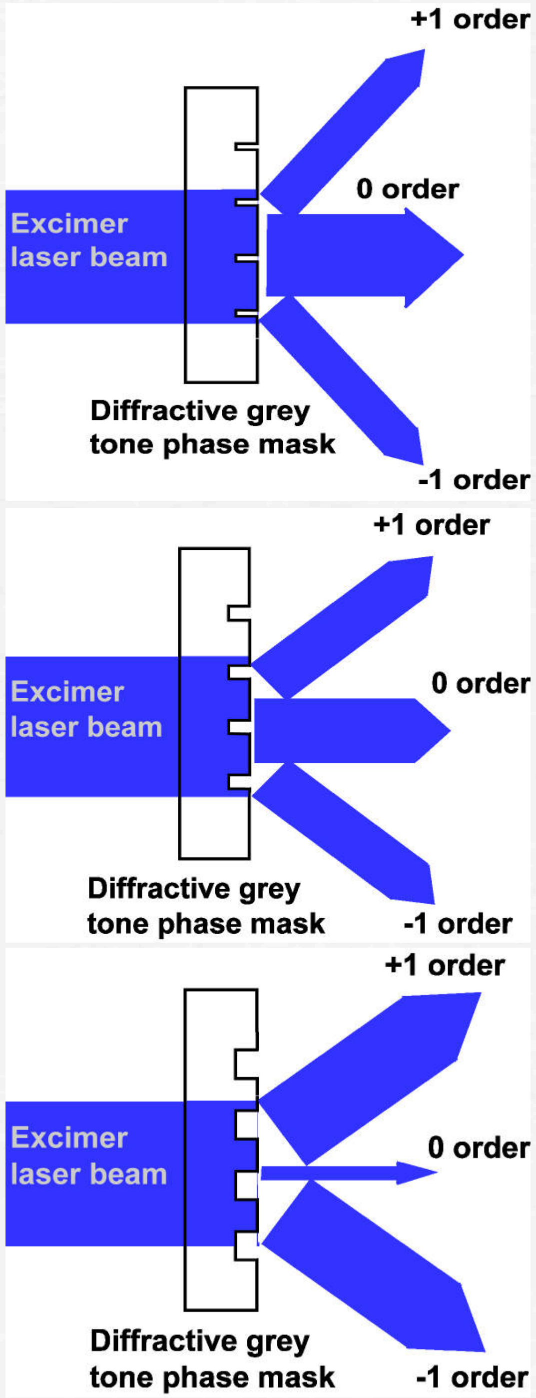
How do we structure a transparent material with a laser?

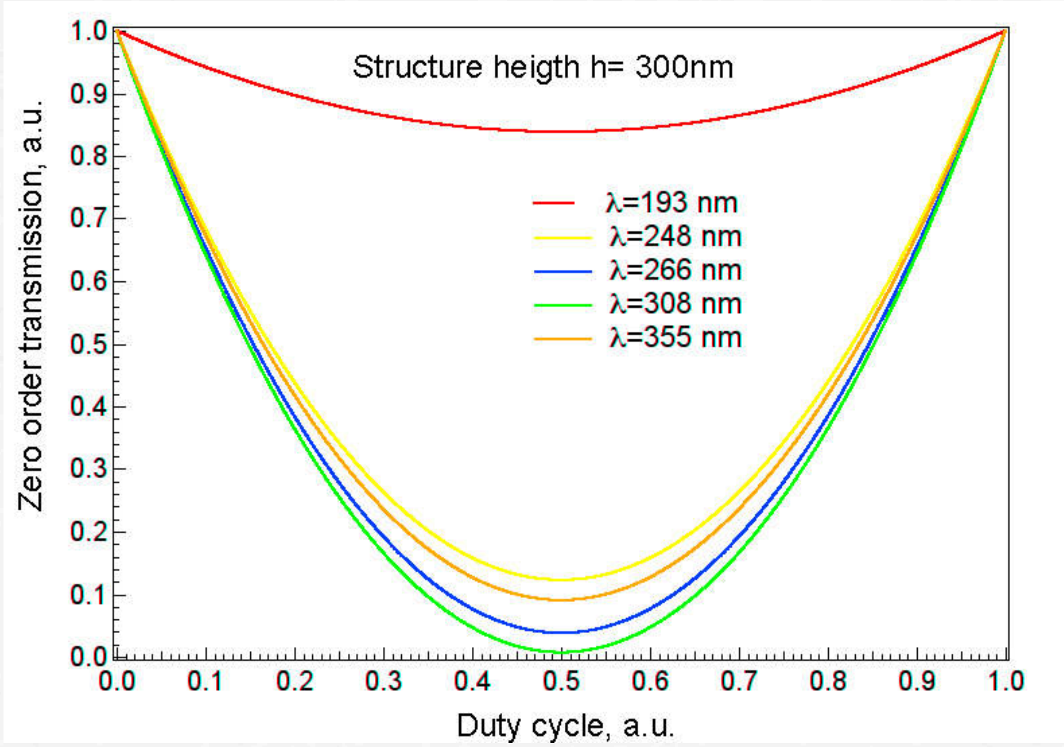
With a fs laser...but we do not have one.....and it has a too small beam anyhow and we want to do 3 dimensional structuring

DGTPM is key: prepared by electron beam lithography and RIE



Diffractive Gray Tone Phase Mask

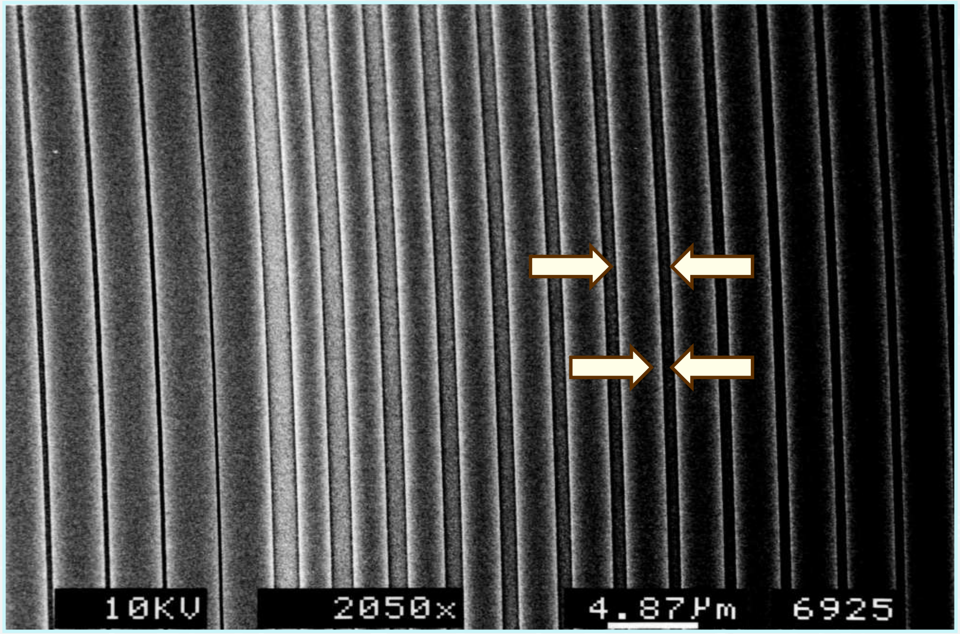




Important for mask design (25000-50000 lines) by E-beam lithography and RIE:

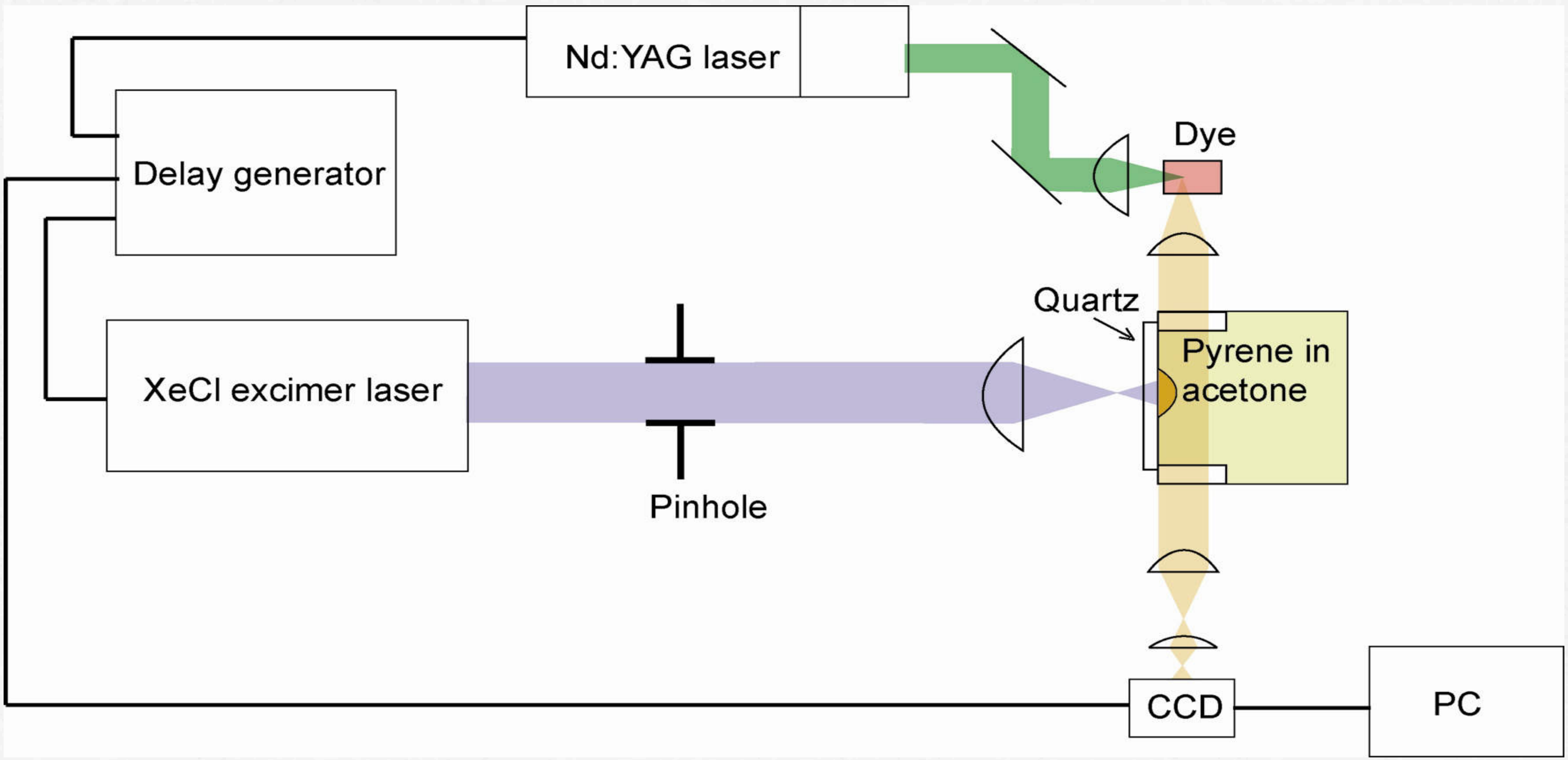
- Threshold fluence
- Non-linear etch rates

$$Duty\ Cycle = \frac{Line\ Width}{Grating\ Pitch}$$

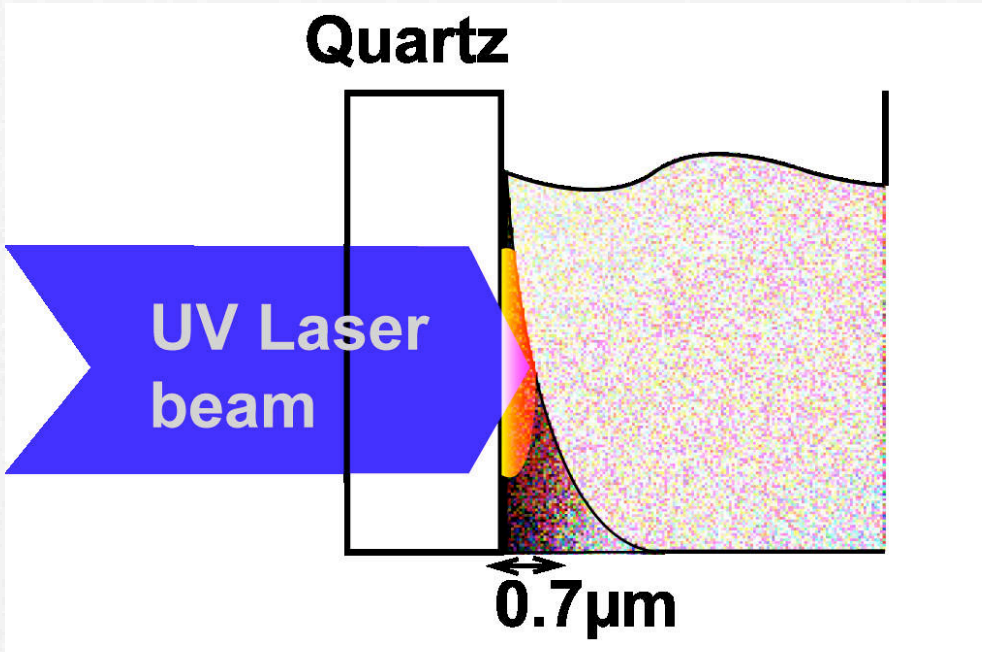


By C. David, PSI

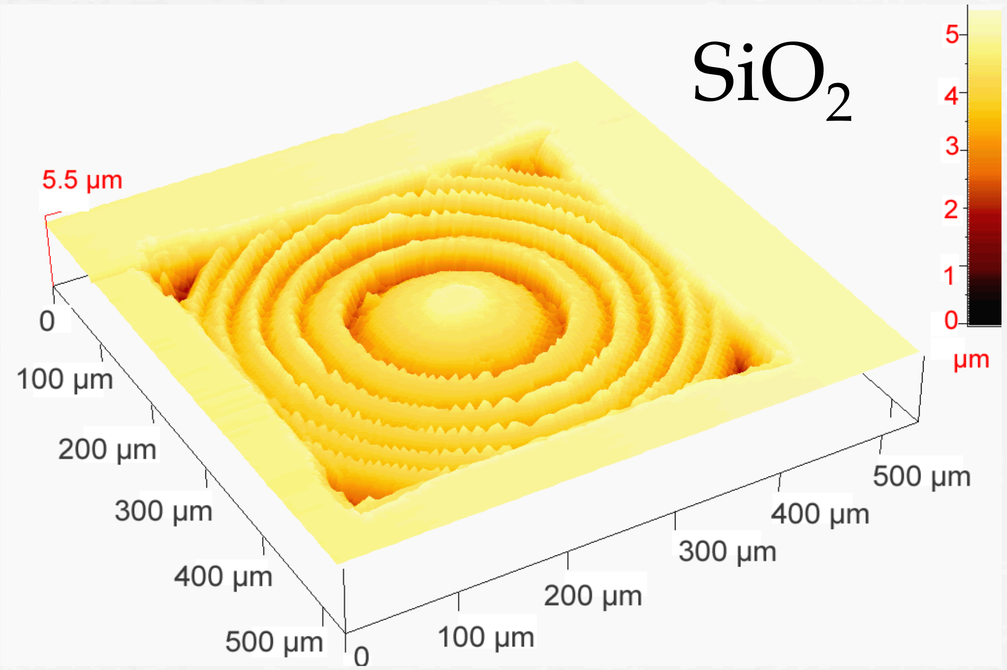
Time-resolved Studies

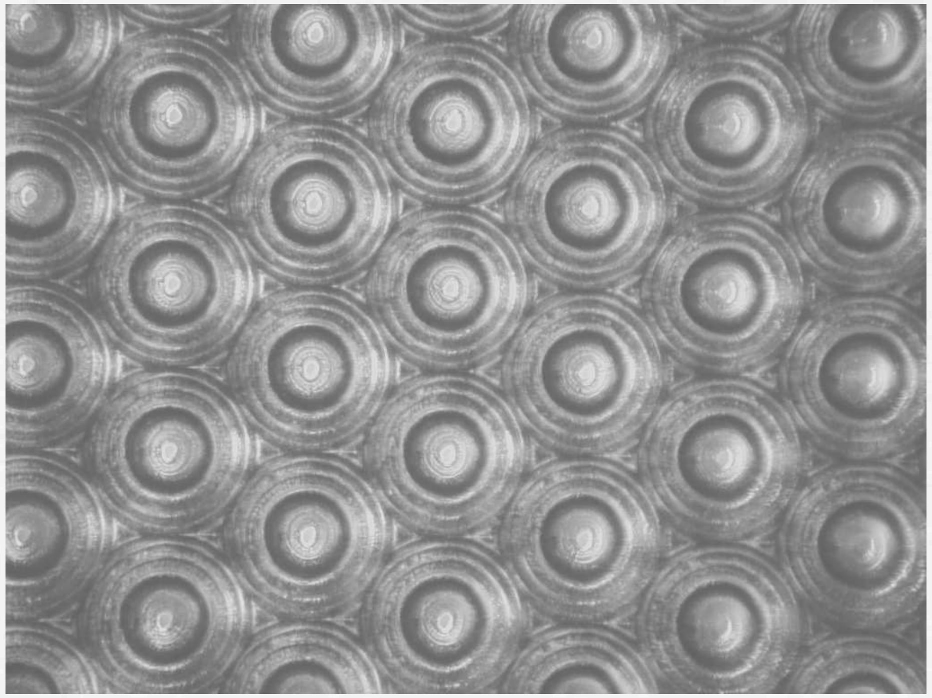


How does it work?

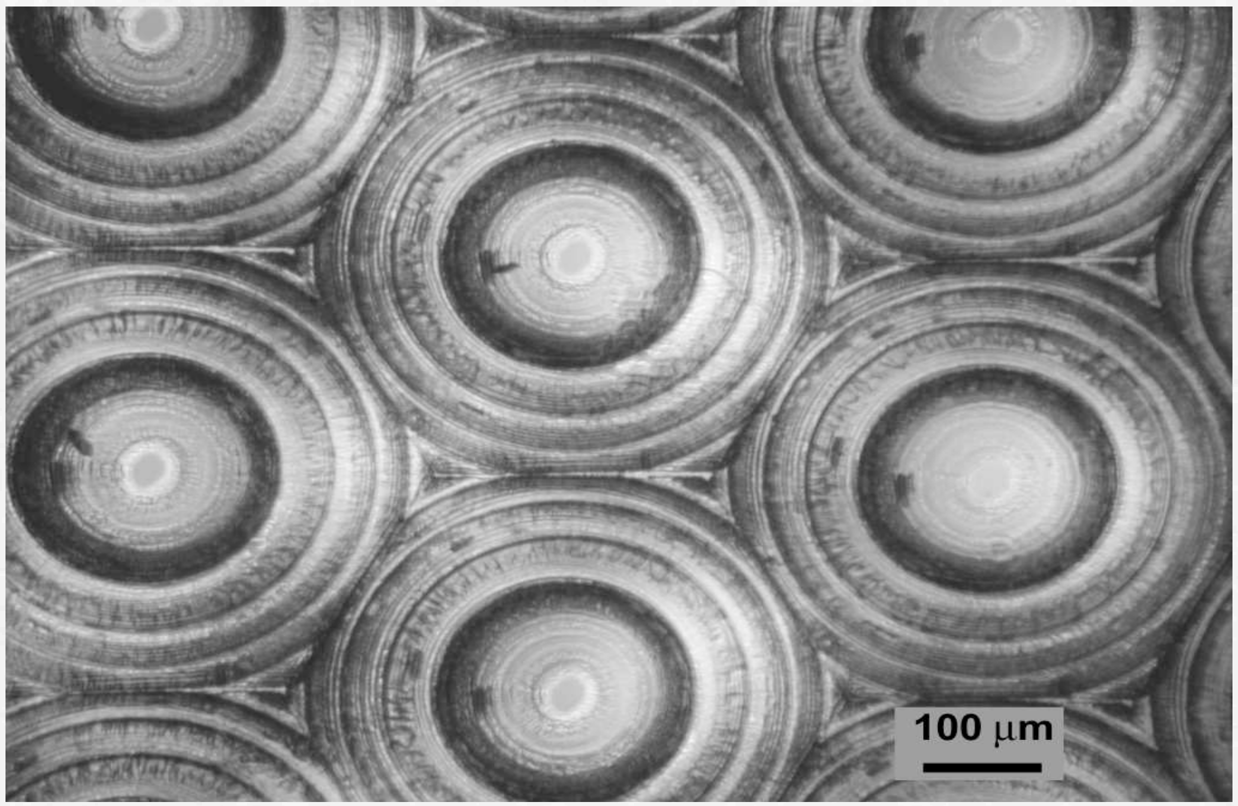


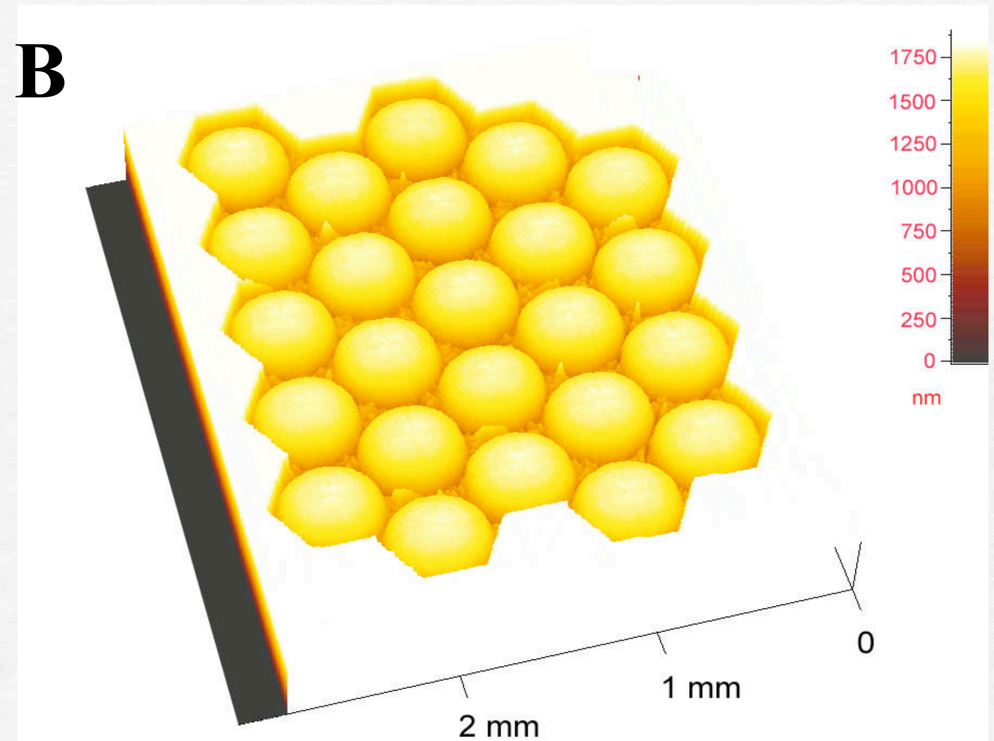
Temperature jump at solid liquid interface (may be reaching the melting T), shock wave, bubble expansion and collapse....not directly related to thermodynamic material properties (melting temperature, thermal conductivity etc.)...may be mechanical properties....but it works!!!!

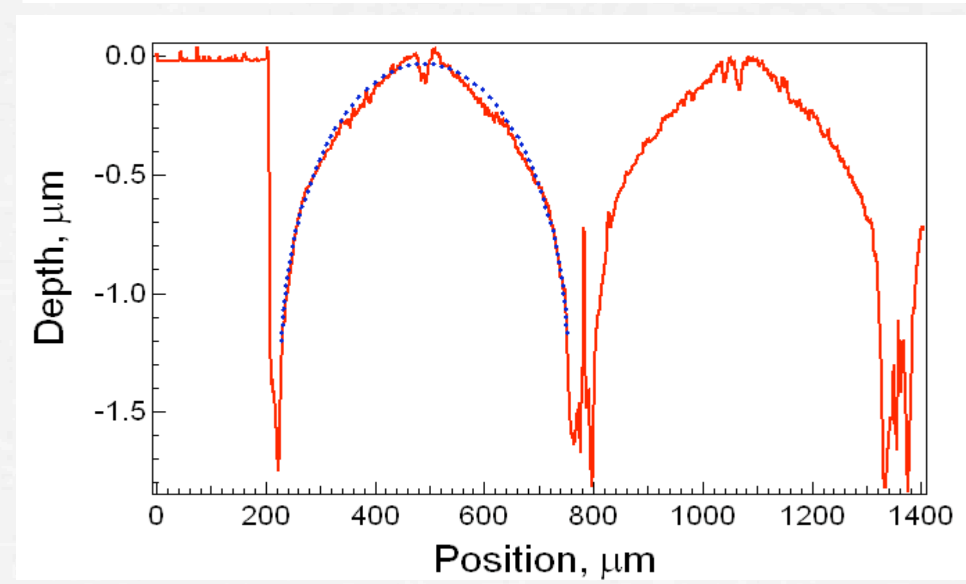




Microlenses in Quartz

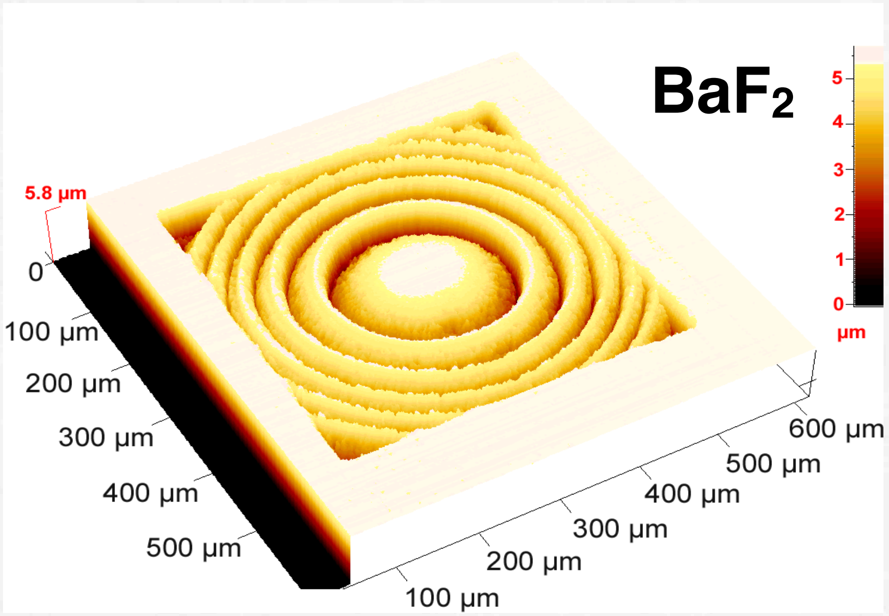






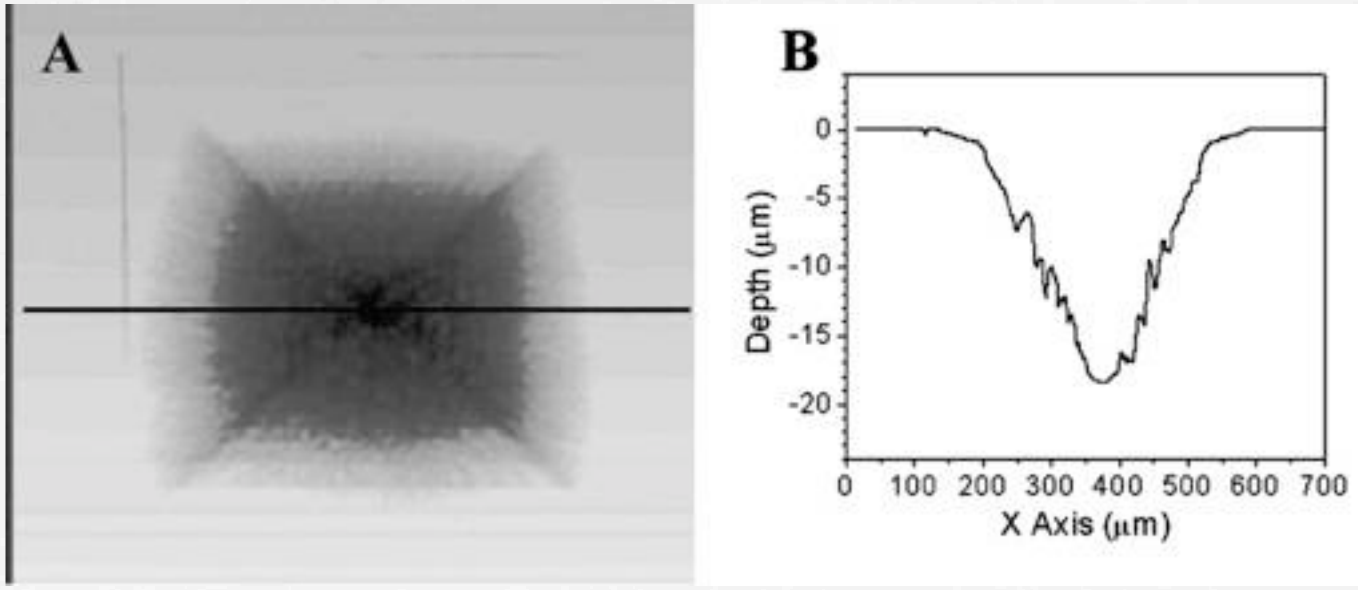
Application as beam homogenizer (ns beams also for Gaussian beams) and DOE

Other materials-other structures



Roughness for etching:

- $SiO_2 \geq 5nm$,
- $BaF_2 = 200$ nm



- Microprism in quartz, image and line scan

Conclusions

- PLD can be used to deposit oxide layers, even possible in micro devices
- New approaches may improve material properties and performance
- Laser direct write techniques are possible alternatives to printing techniques.
- A wide variety of materials can be transferred
- The application of a dynamic release layer (absorbing layer) increases the possibilities for laser direct write methods.
- It is possible to deposit even functional layers in "devices"
- Even "transparent" materials can be structured with shaped beams to yield, e.g. functional micro-optics