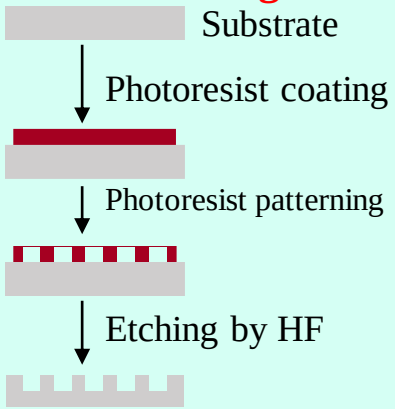
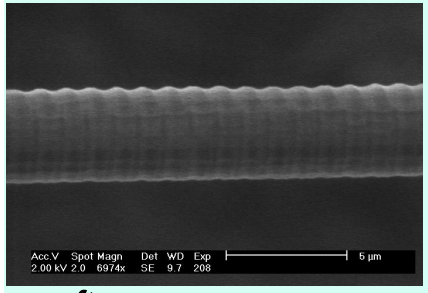
GLASS MICROSTRUCTURING

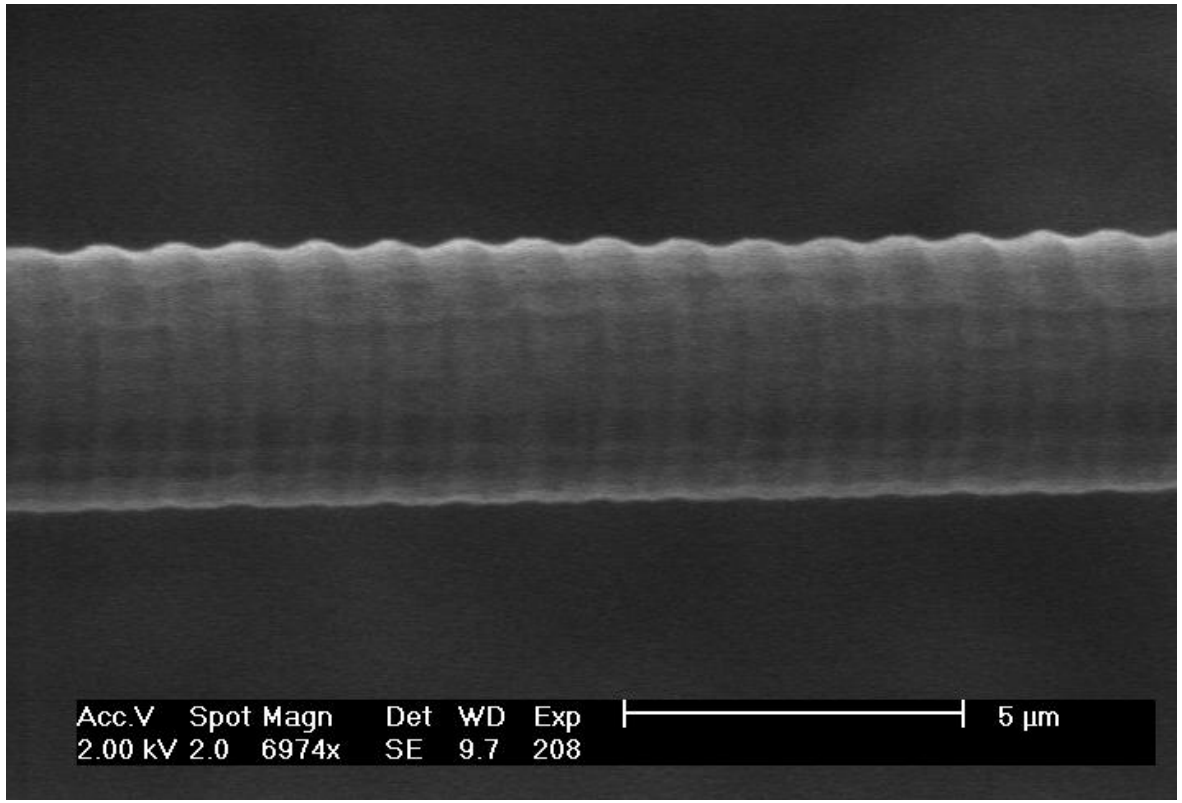
Wet Etching



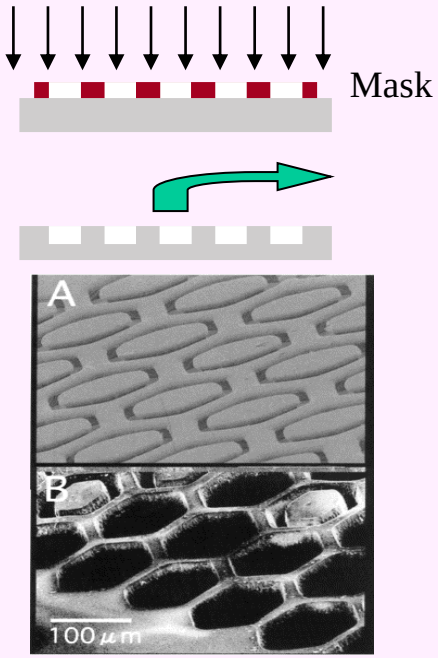


Advantage
- Good resolution

Disadvantage
- Low aspect ratio
- Slow speed
- Toxic chemicals



Dry Etching

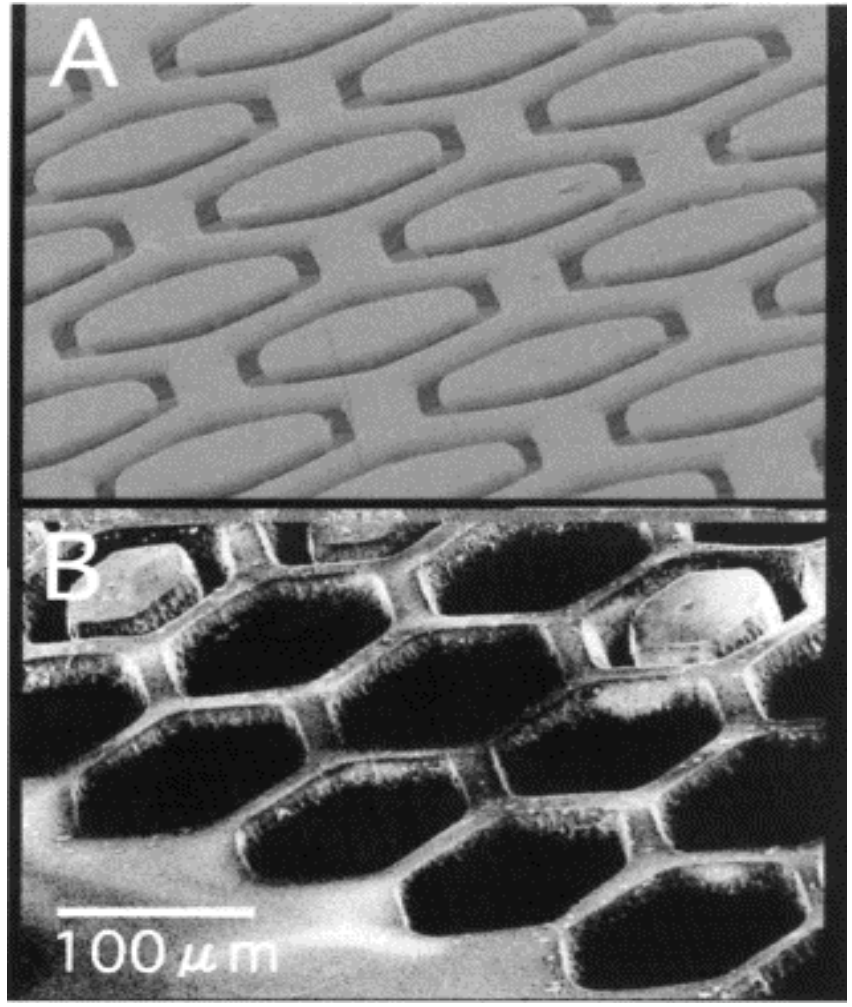


Advantage

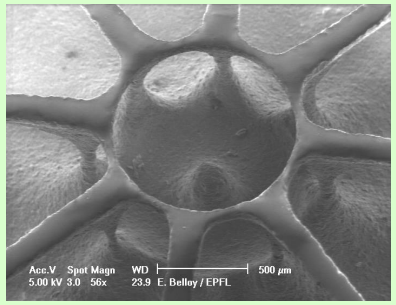
- High Aspect ratio

Disadvantage

- Low resolution
- Volatile formed



Powder Blasting

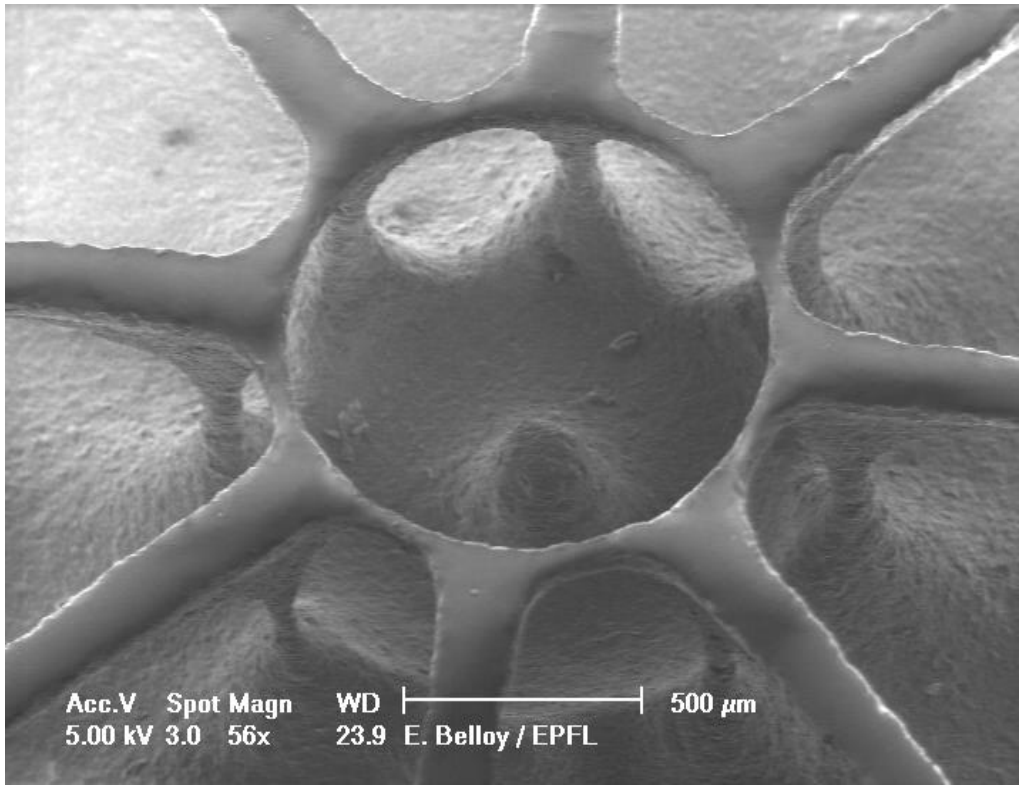


Advantage

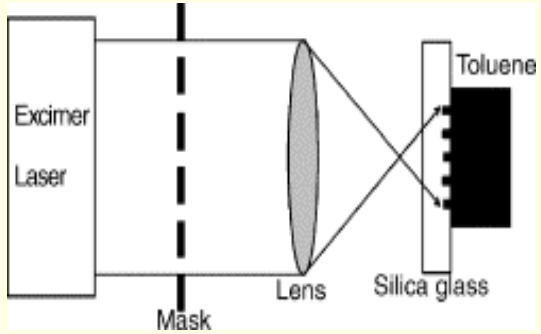
- Fast Erosion Rate
- High Aspect ratio

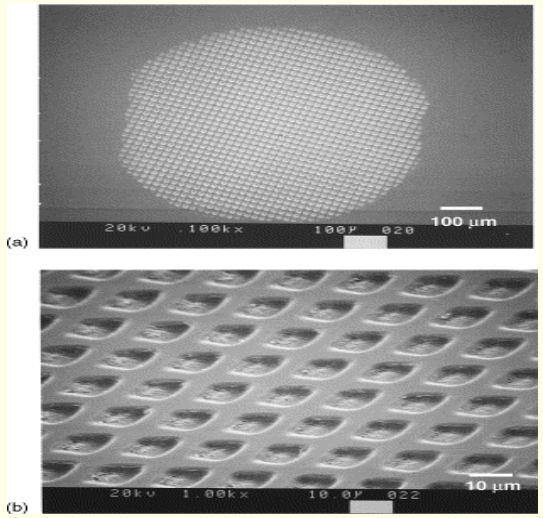
Disadvantage

- Low Resolution
- Very Rough Surface



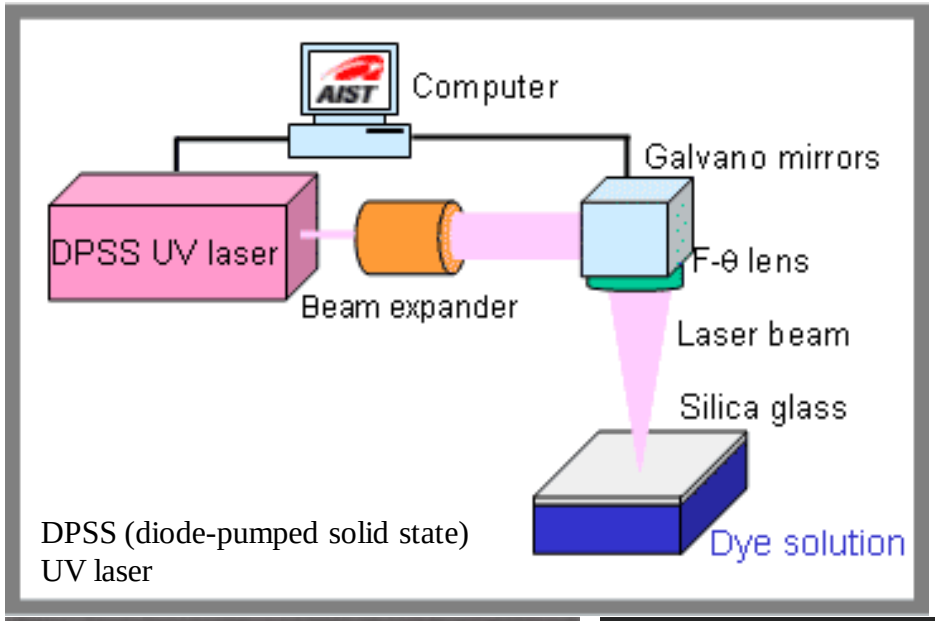
LIBWE



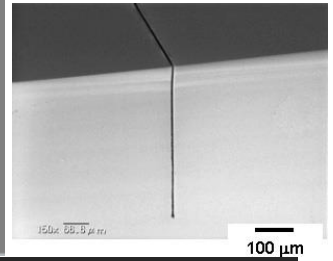


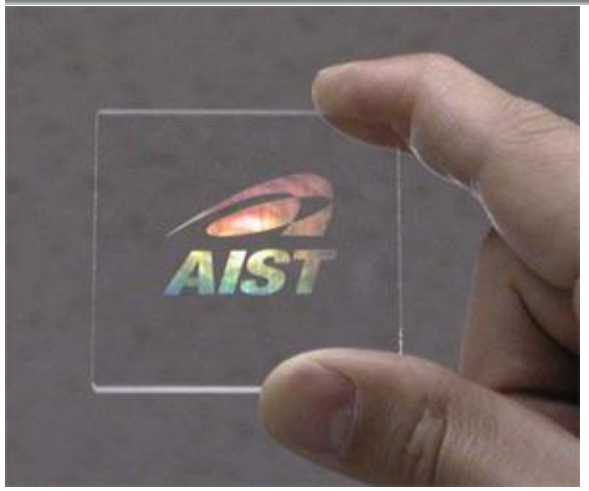
Advantage

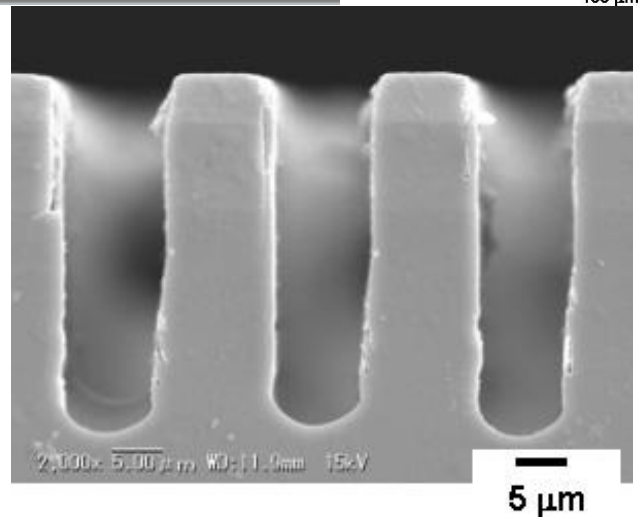
- Good resolution



DPSS (diode-pumped solid state) UV laser

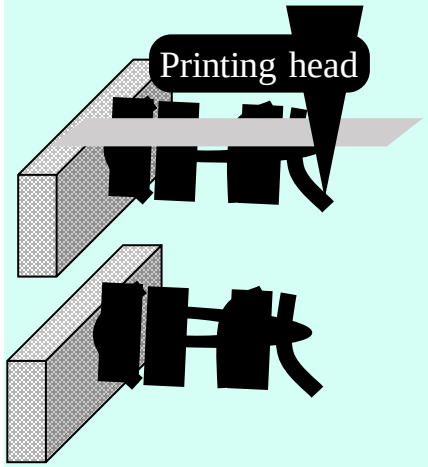






DEPOSITION

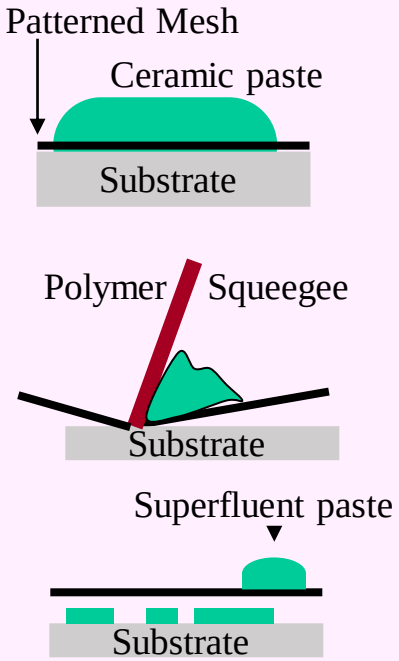
Suspension printing



Advantage
- Dense structure

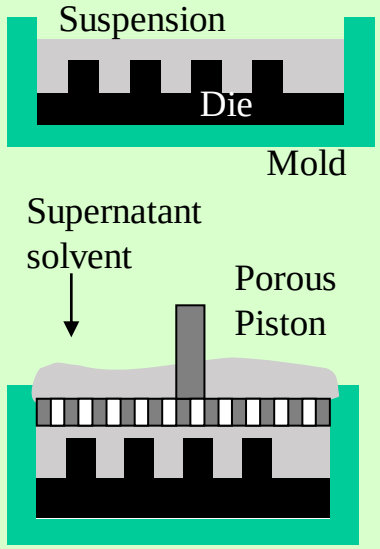
Disadvantage
- Low resolution
- Low aspect ratio
- Very slow speed
- Pattern over porous substrate only

Screen printing



Disadvantage
- Low resolution
- Small aspect ratio

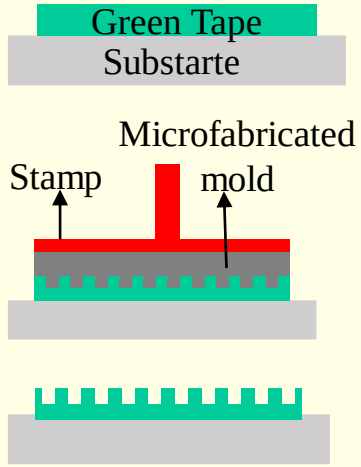
Filter Pressing with a porous piston



Advantage
- High Aspect Ratio

Disadvantage
- Low resolution
- Mold removal

Tape embossing

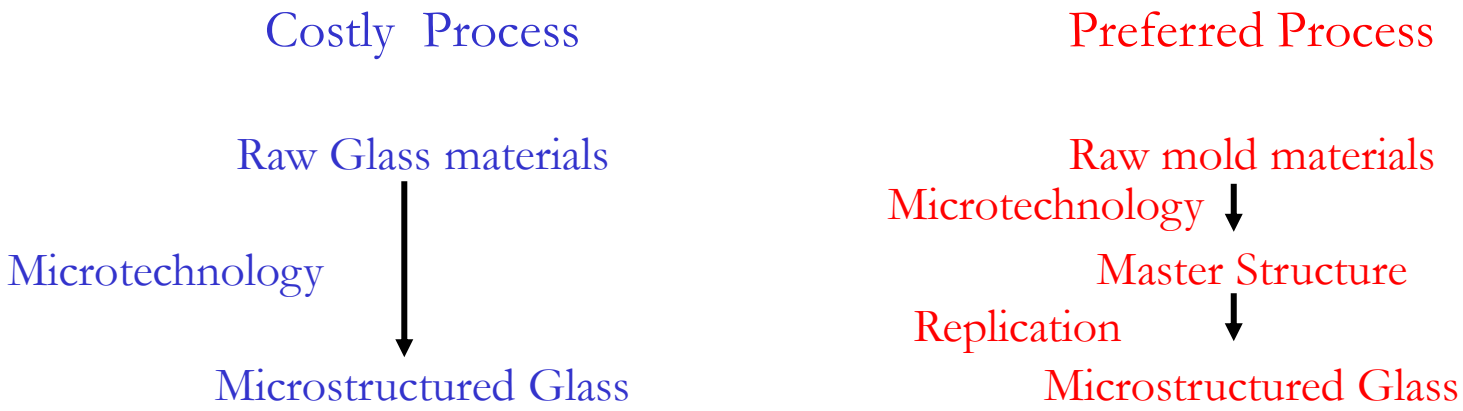


Advantage
- High aspect ratio
- Reusable mold

Disadvantage
- Low resolution
- Demolding problem

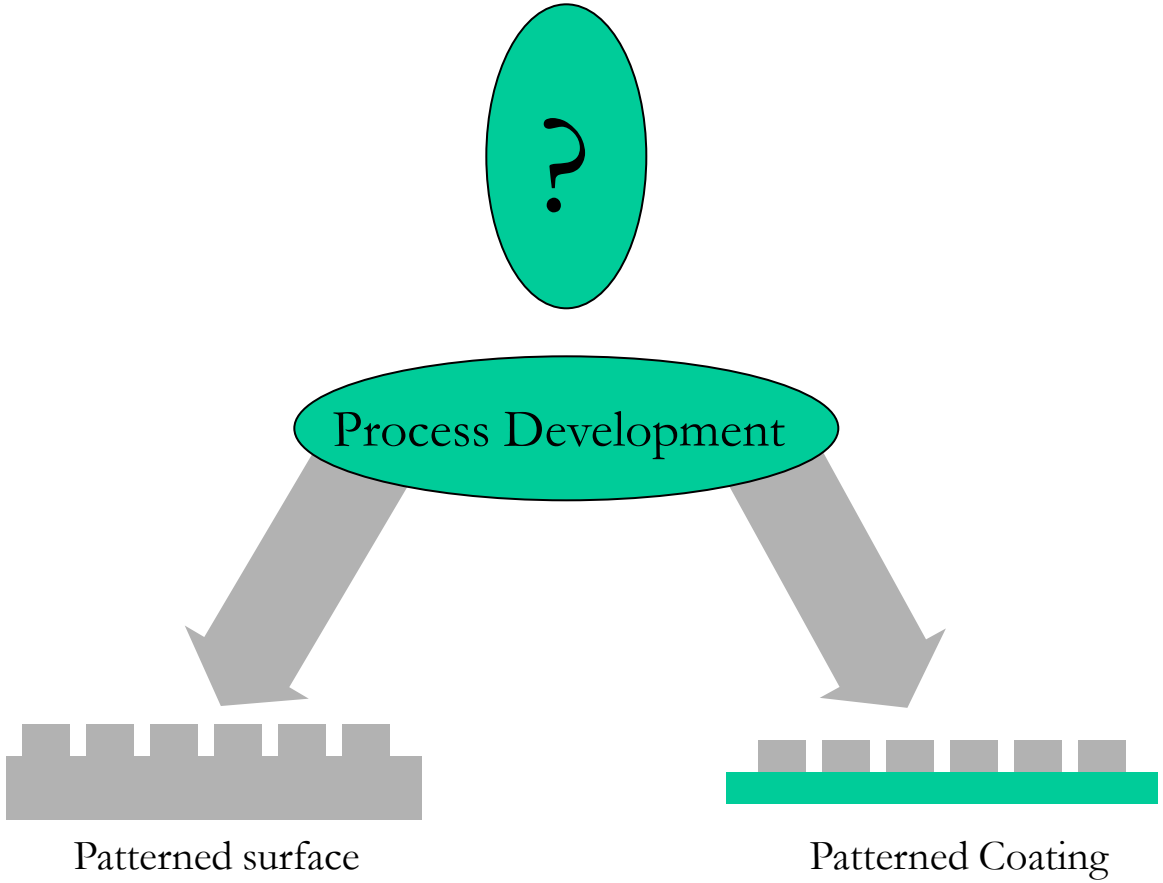
Replication

Replication of Micro-structures

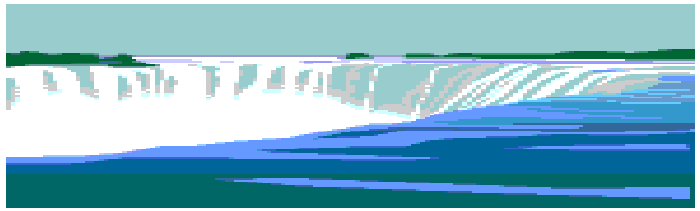


Creating a master with microtechnology and replicating it with macrotechnology is preferred

Replication of Micro-/Nano- structures



Fundamental requirement



Transition of physical state

Glass melt

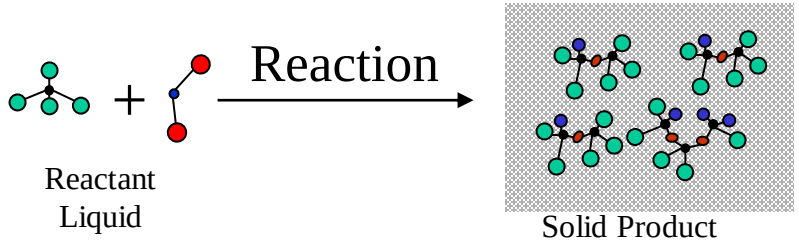
COOLING

Liquid Precursor

Chemical Reaction

Process Development

A Chemical Reaction



Reactant : Alkoxide

Product : Oxide

SOL GEL PROCESS

Sol Gel Process

Sol

Stable dispersion of solid particles in Brownian Motion with in a liquid matrix.

Gel

3-Dimensionally interconnected solid network that expands in a stable fashion throughout a liquid medium and is only limited by the size of the container.

Gelation

Process of transformation from viscous liquid state to solid phase

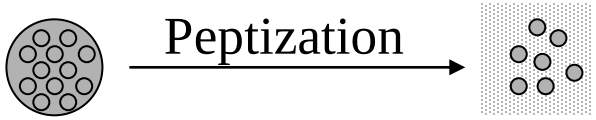
Definition of Sol-Gel Process

Formation of 3-Dimensional amorphous polynetwork of metal oxide through the gradual transition from liquid (Sol) to solid (Gel) phase

Sol Gel Process

- Colloidal Route

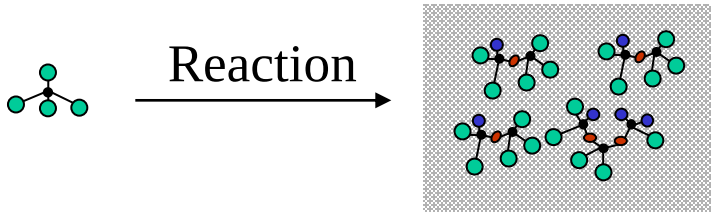
  Suspension of active oxide particles of dimension between 1nm to 1μm



  Stability : control the physical aggregation of colloidal particles

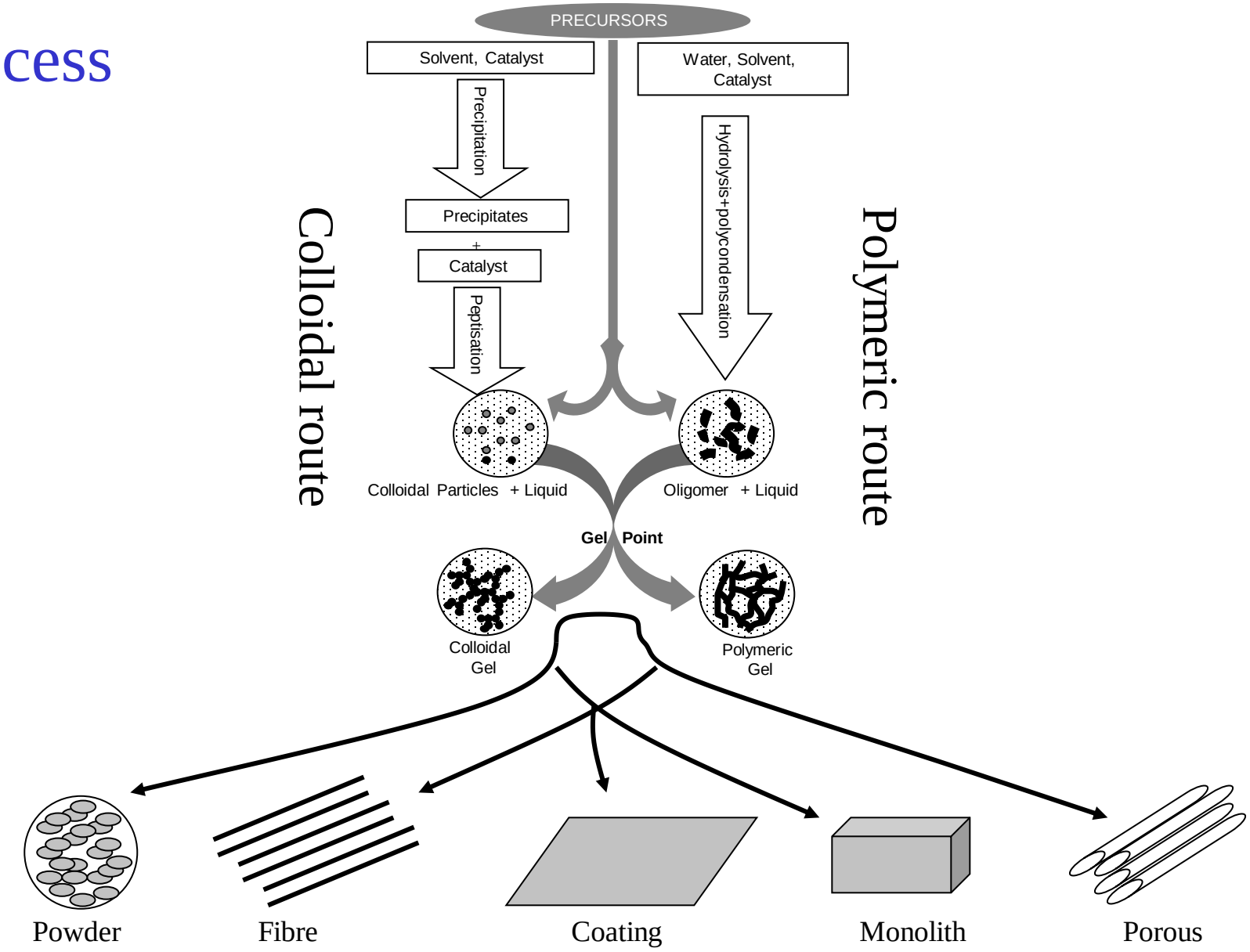
- Polymeric Route

  Suspension of oligomeric units in a liquid matrix



  Stability : Control the chemical bond formation

Sol Gel Process



Sol-Gel Process (parameters)

$$A + H_2O + Catalyst \xrightarrow{\text{Chemical Reaction}} Sol \xrightarrow{\text{Drying conditions}} Gel$$

Parameters

- Water content,
- Catalyst,
- Concentration,
- Temperature,
- Drying conditions

Sol Gel Process (Effect of parameters)

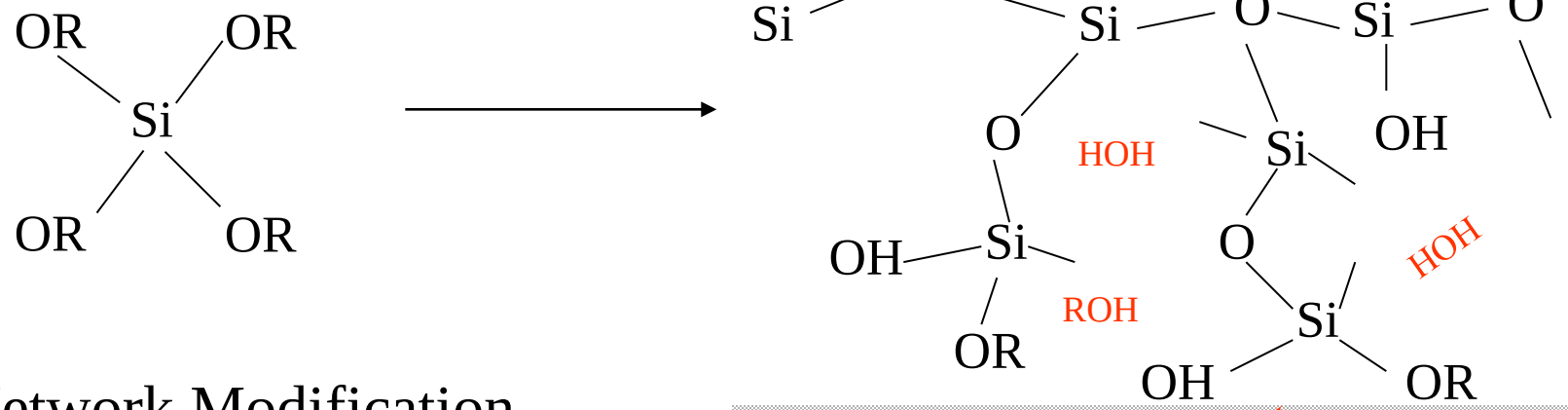
- Acid-catalyzed
  - yield primarily linear or randomly branched polymer

- Base-catalyzed
  - yield highly branched clusters

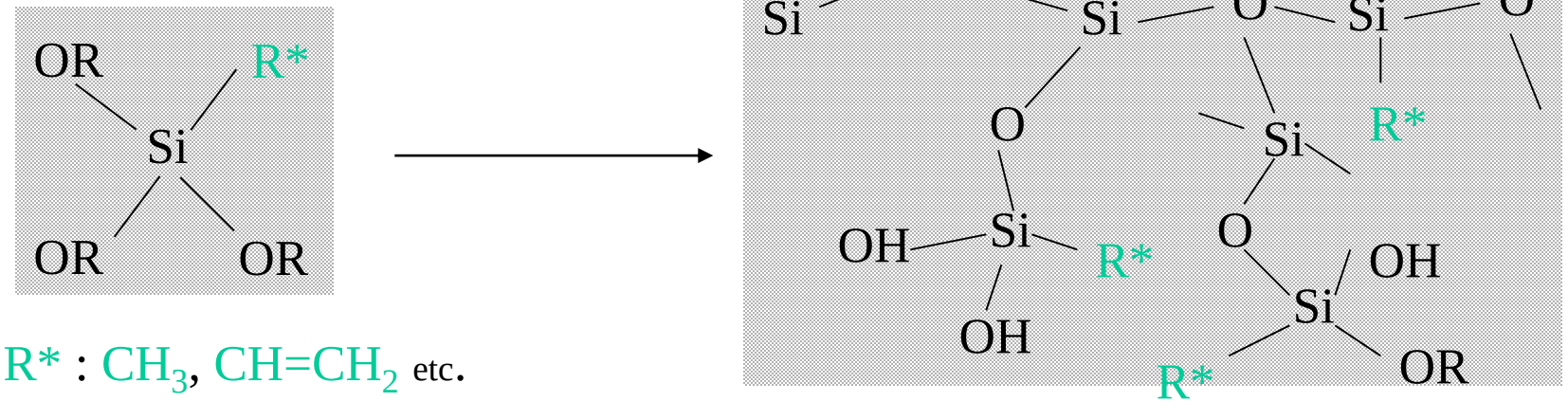
- Higher water content, high concentration of HCl and base catalysis lead to completely polymerised three dimensional gel network

Sol-Gel Process

Network Formation



Network Modification



R* : CH_3, $CH{=}CH_2$ etc.

Sol-Gel Process (Adv. & Disadv.)

Advantages

Less energy consumption,
Better homogeneity
Higher purity
Extended composition range

Drawbacks

Time Consuming
Dimensional Change
Stress Cracking

Sol-Gel Process – Main Adv.

Main Advantage

Dielectric property

- Low k material
- High k material

Low k material

Low k material requirements

Electrical Properties

- ❖Reduced dielectric constant (k_{SiO_2} ~ 4)

Physical properties

- ❖ Mechanical strength
- ❖ Adhesion to oxides, nitrides, metals
- ❖ Low intrinsic stress

Chemical properties

- ❖ Chemical stability
- ❖ Thermal stability

How to design ?

Compositional changes

- ❖ Less polarizable bonds

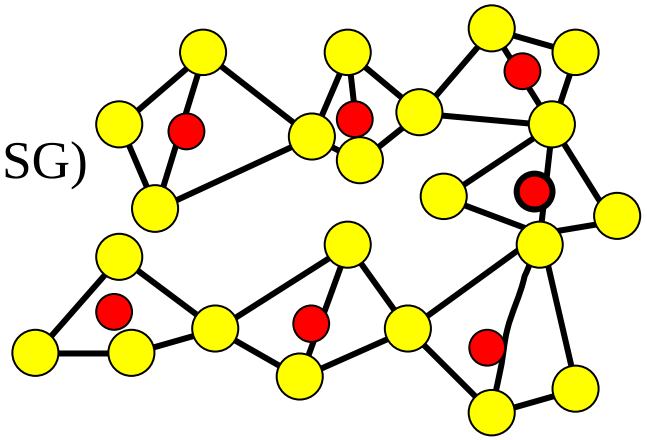
Reduction of density

- ❖ Change network structure (via addition of terminal bonds)
- ❖ Introduction of porosity

These changes while reduce the dielectric constant, can degrade the mechanical properties

Low k material

- Reduce the density by breaking up SiO2 network
- Introduce terminal groups that can not network
  - ➢F (to form fluorosilicate glass FSG)
  - ➢CH3 (to form an Organosilicate glass OSG)



Physical structure of Silica
(Basic unit SiO_4 Tetrahedra)

In addition to reduce density :

- Fluorine also lowers the electrical polarizability
- Organic groups replacing O atoms lowers the ionic contribution to k

High k material

Higher k films ⇒ Thicker gate dielectric ⇒ lower leakage and power dissipation with the same capacitance

Dielectric Constant	Dielectrics
10 ~20	$ZrSi_xO_y$, $HfSi_xO_y$, $LaSi_xO_y$ $ZrAl_xO_y$,ZrN_xO_y
15 ~30	ZrO_2, HfO_2,La_2O_3,Y_2O_3

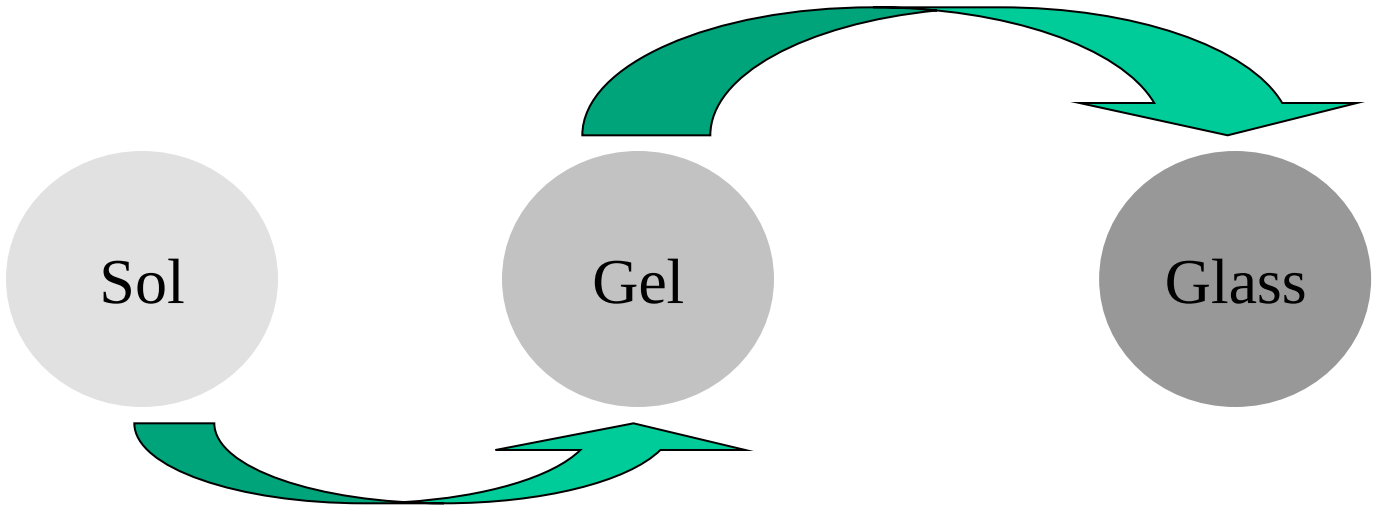
High k material (Deposition methods)

- ✓ Metal organic chemical vapor deposition (MOCVD)
- ✓ Physical vapor deposition (PVD) [sputtering,evaporation]
- ✓ Atomic layer deposition (ALD)
- ✓ Molecular beam epitaxy(MBE)

New Approach is SOL-GEL Processing

Structure of Sol Gel Glass

- Structure of sol gel derived glasses evolves sequentially as the product of successive hydrolysis and condensation reactions.



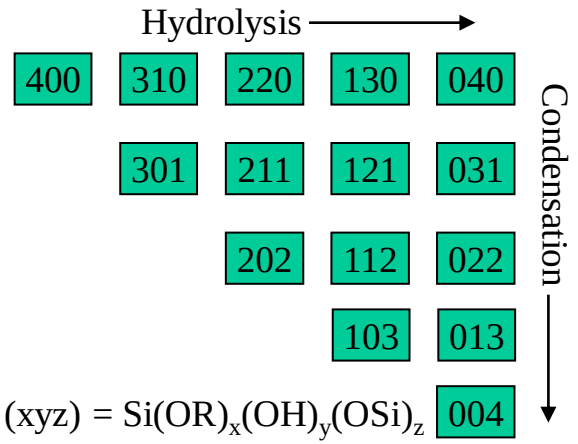
Structure of Sol Gel Glass

- Stage I – Sol to Gel

Shortest Length Scale

Nearest neighbor of metal atom may be

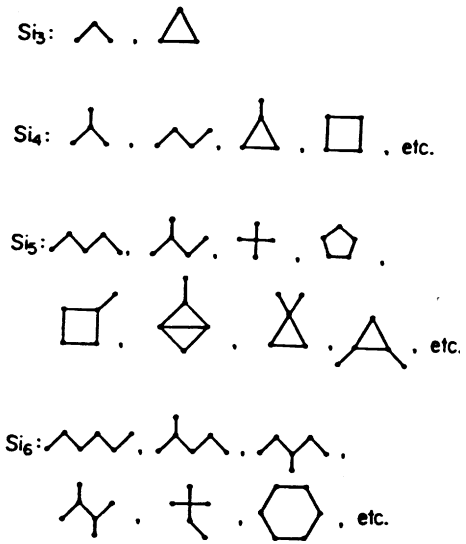
i. An alkoxide group
ii. A hydroxyl group
iii. Bridging oxygen



Intermediate length scale

Oligomer species

i. Dimer
ii. Trimer
iii. Tetramer etc.

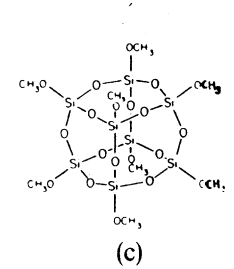


Possible siloxane framework. Vertics represent silicon and line represent oxygen centre brdge to two silicon atom

Larger scale

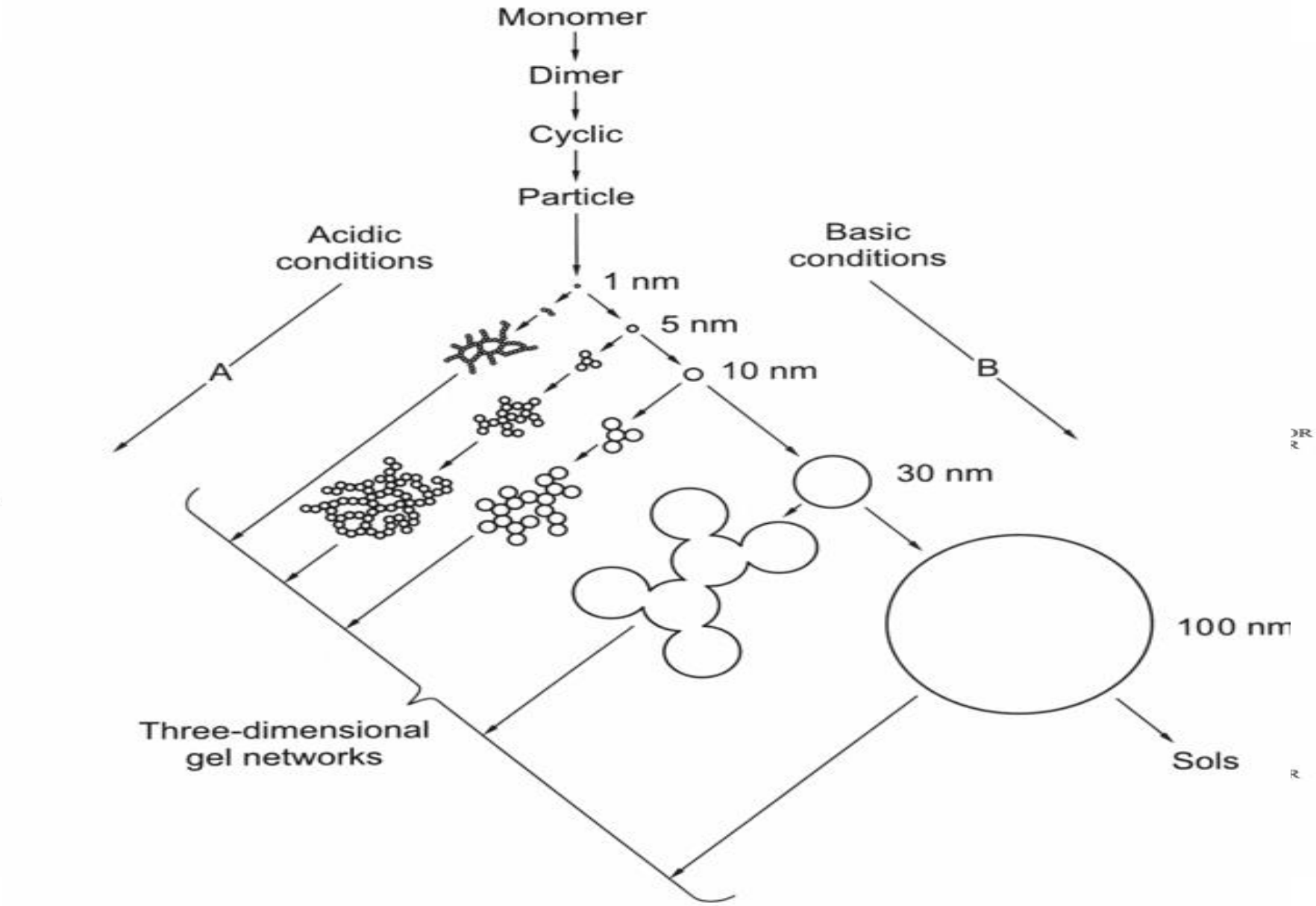
Well defined solid to liquid interface

i. Linear
ii. Branched
iii. Cyclic



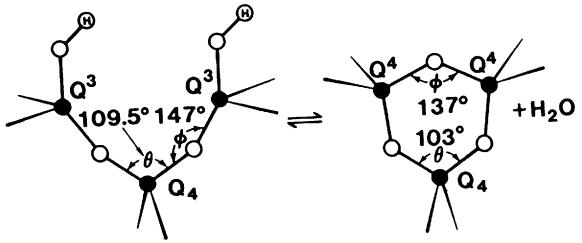
(c)

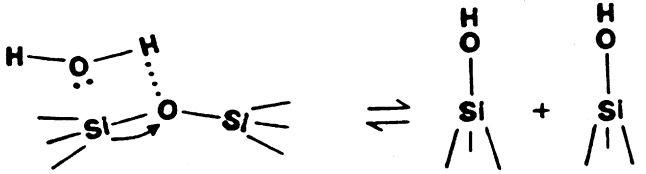
Structure of Sol Gel Glass



Structure of Sol Gel Glass

- Structural development during consolidation
  - Q^4 silicon sites are very similar to fused silica
  - Physical properties (density, refractive index, thermal expansion, modulus) nearly identical to fused silica





Cyclic bond formation and debonding

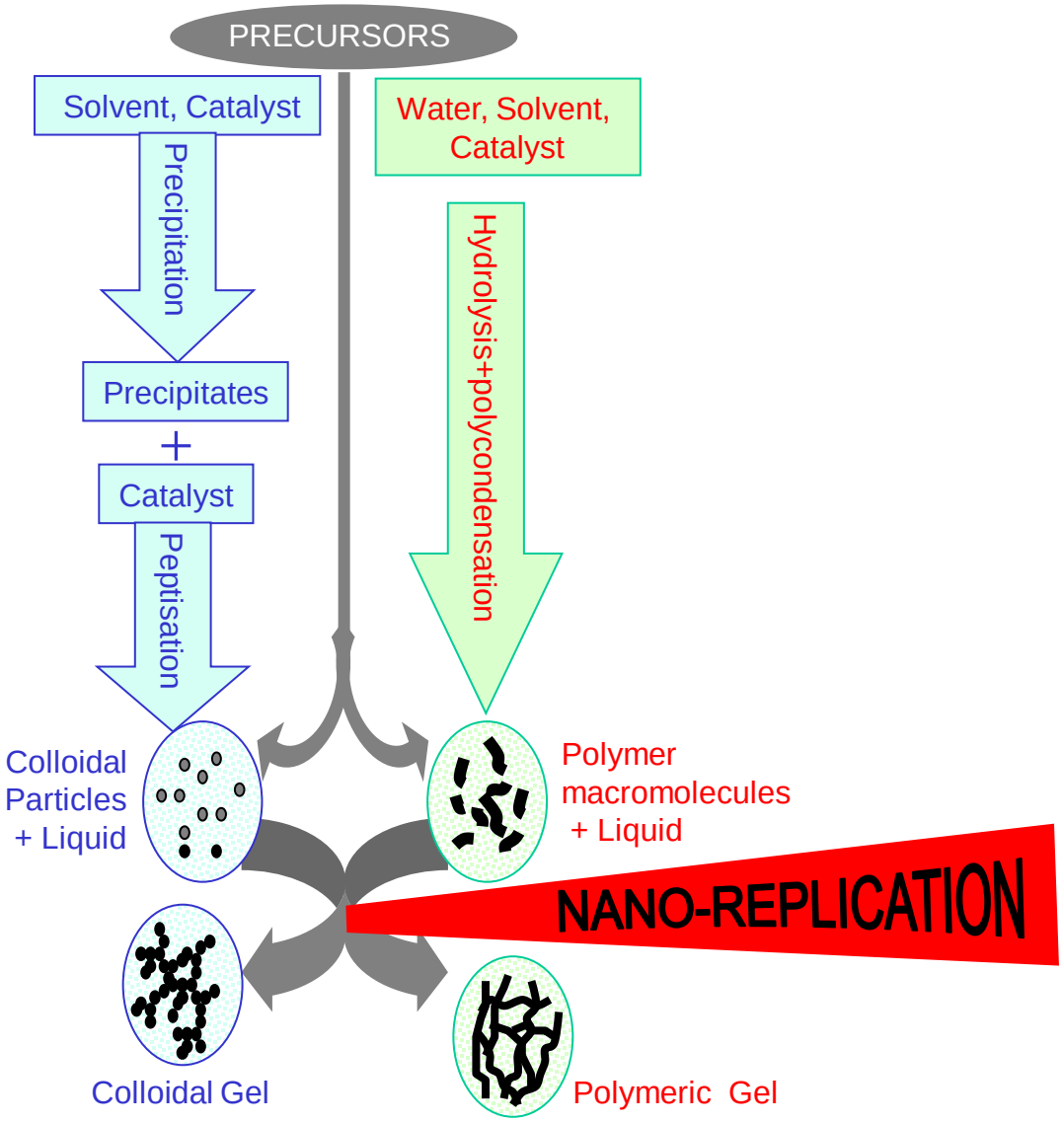
Replication of Micro-/Nano- structures

Sol-Gel Process : A true liquid –solid transition

A good replication route

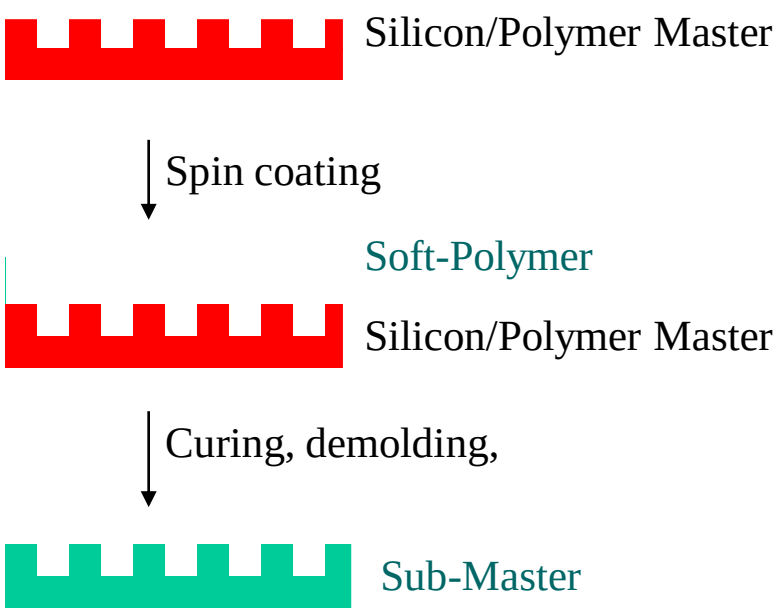
Desired Properties of Glass in nano-structures can be achieved

Replication of Micro-/Nano- structures

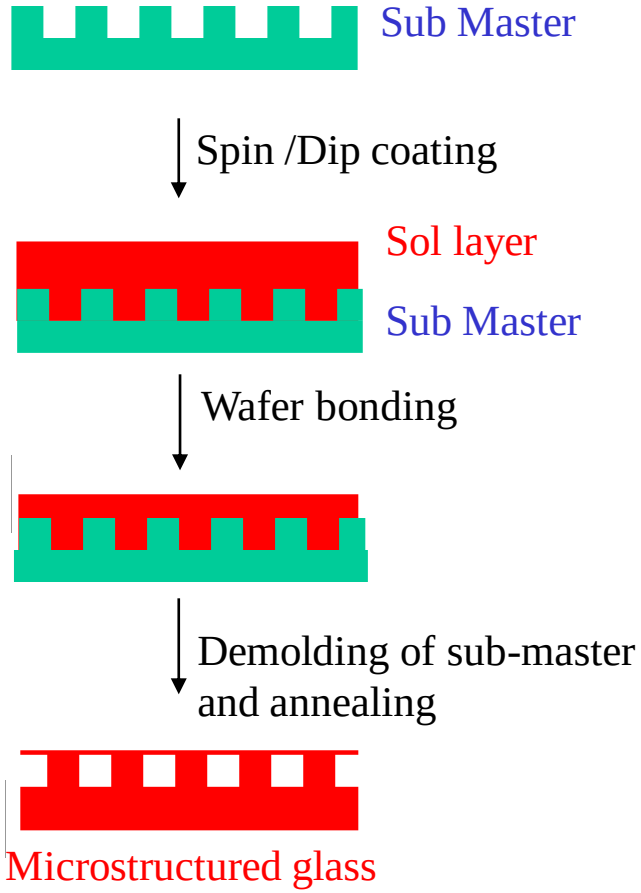


Replication of Micro-/Nano- structures

Fabrication of Sub-Master



Replication in Glass



Replication of Micro-/Nano- structures

Soft-Polymer Sub Master

Fabrication of Soft polymer ‘Sub-Master’ using ‘Silicon Master /PMMA Master’

PDMS : SylGard 184,

Mixing Ratio	10:1
Curing Temp.	60° C
Curing time	24 Hrs

Polyimide : PI 2611

Thermally cured polyaromatic imide

Curing Temp	150° C
Curing time	2 Hrs

PMMA

Materials used for synthesis :

Methylmethacrylate

Triethyleneglycol dimethacrylate

Process:

Polymerisation at room temperature under nitrogen atmosphere using benzoyl peroxide as catalyst and N,N dimethyl aniline as activator

Replication of Micro-/Nano- structures

Post-Replication process

Aging and Drying (Syneresis Process)

Ageing at Room Temperature for two days
Drying at 50°C for 20-25 Hrs.

Heat treatment

Heat treatment to 200°C and 400°C at a rate of 1°C/min.

Physico-chemical changes occur

Pyrolysis of organic groups

$Si\text{-}OC_2H_5 + 3O_2 \rightarrow SiOH + 2CO_2 + 2H_2O$

$Si\text{-}OC_2H_5 + SiOH + 3O_2 \rightarrow SiOSi + 2CO_2 + 3H_2O$

$Si\text{-}CH_3 + 2O_2 \rightarrow SiOH + CO_2 + H_2O$

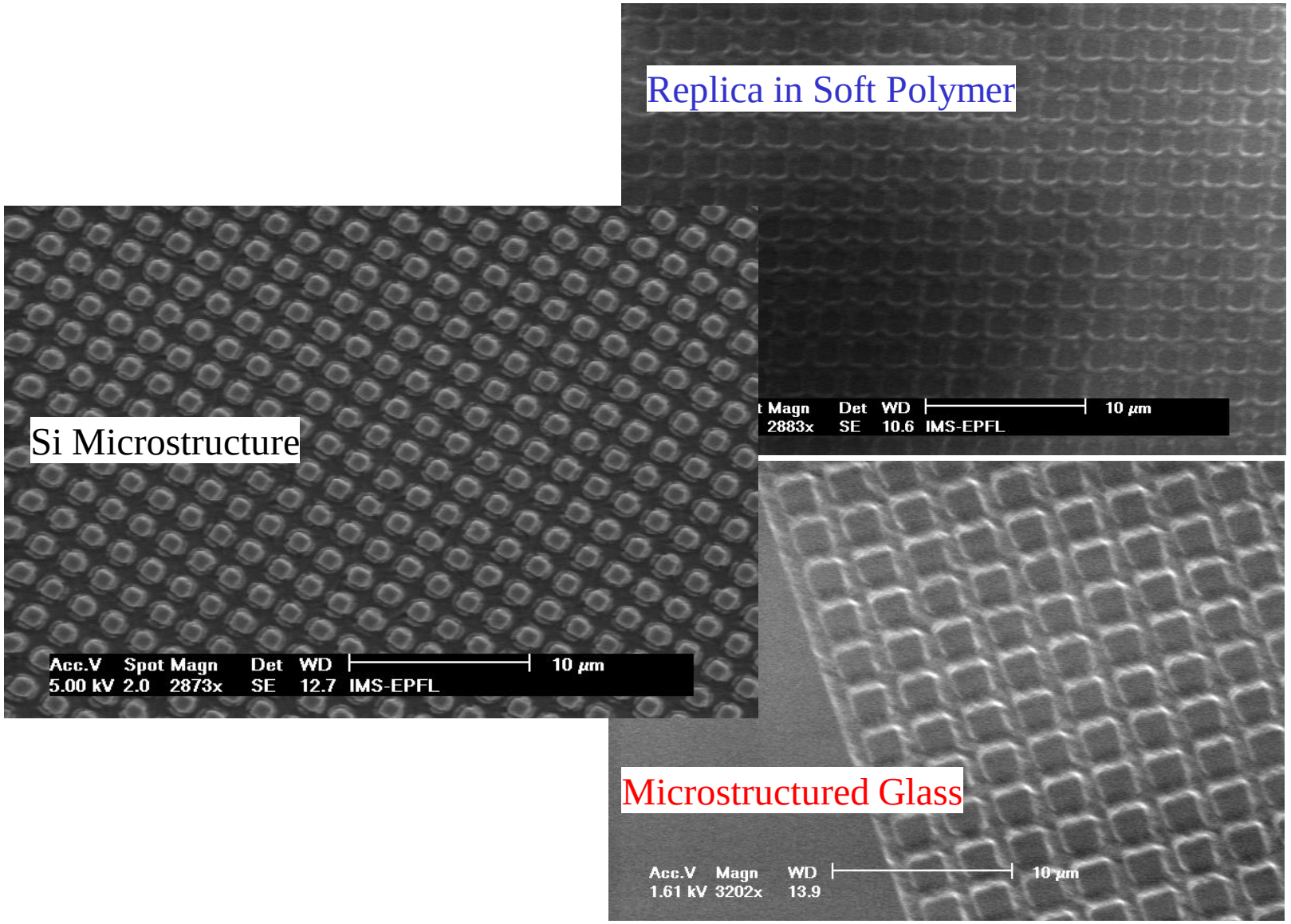
$Si\text{-}CH{=}CH_2 + 3O_2 \rightarrow SiOH + 2CO_2 + 2H_2O$

$Si\text{-}OH + Si\text{-}OH \rightarrow Si\text{-}O\text{-}Si + H_2O$

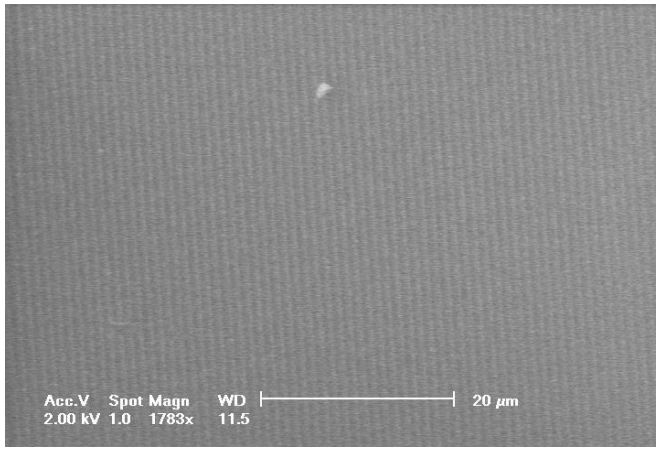
Shrinkage

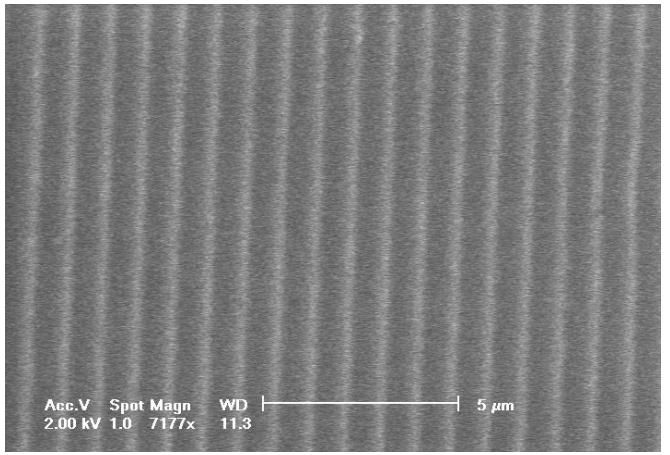
Strengthening

Replication of Micro-/Nano- structures

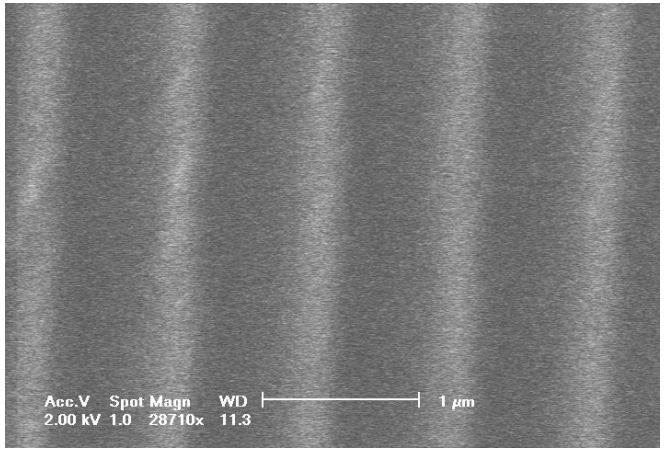


Replication of Micro-/Nano- structures

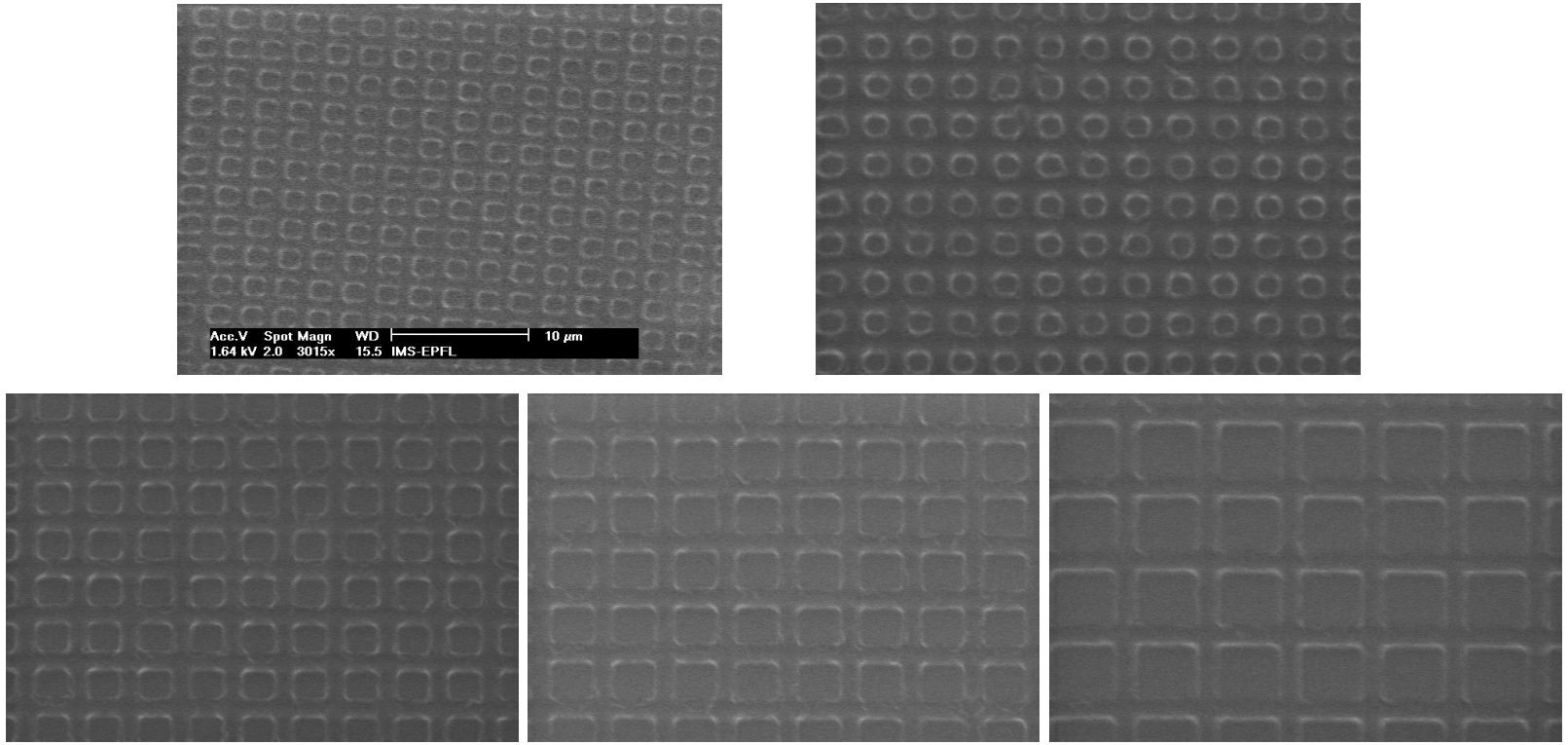




SEM photographs of
1 micron holographic gratings
(annealed stage)

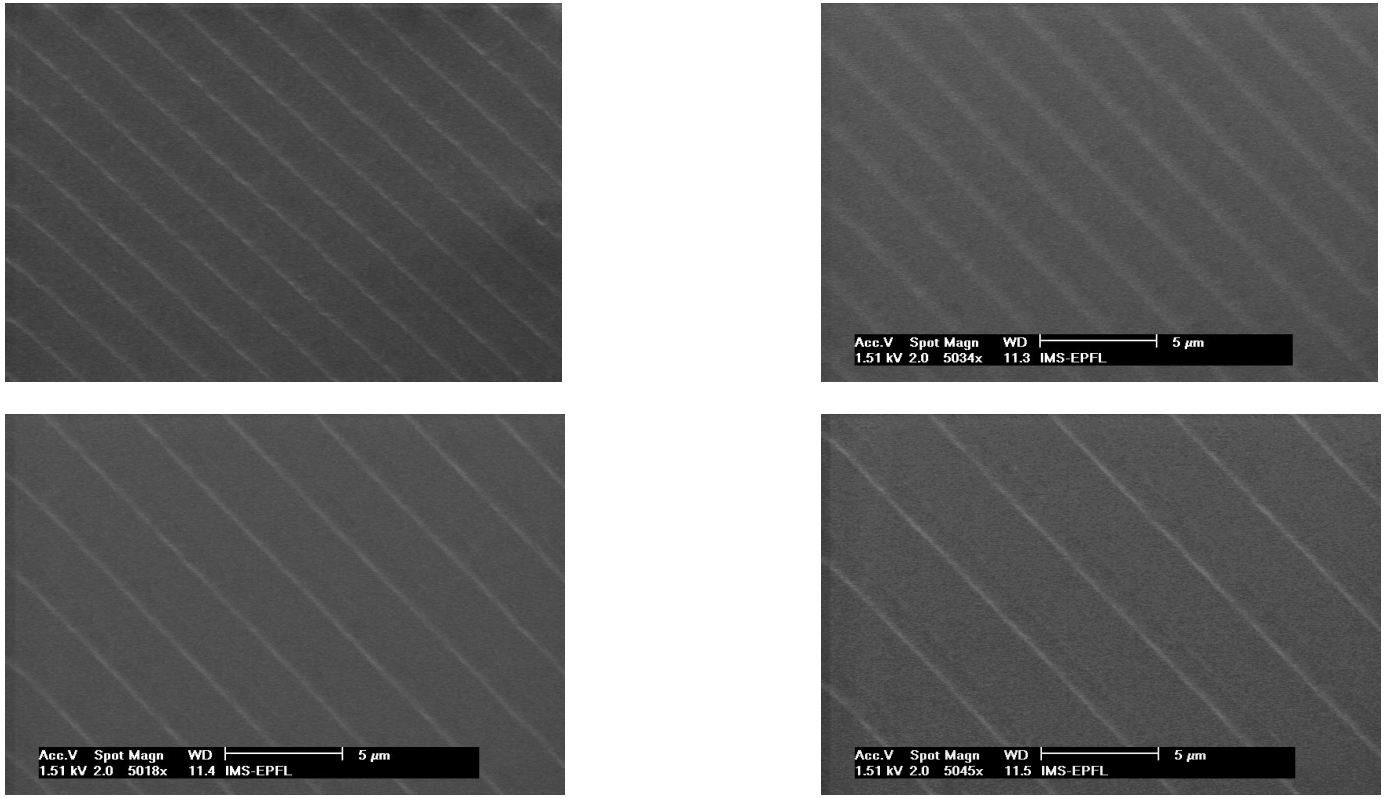


Replication of Micro-/Nano- structures



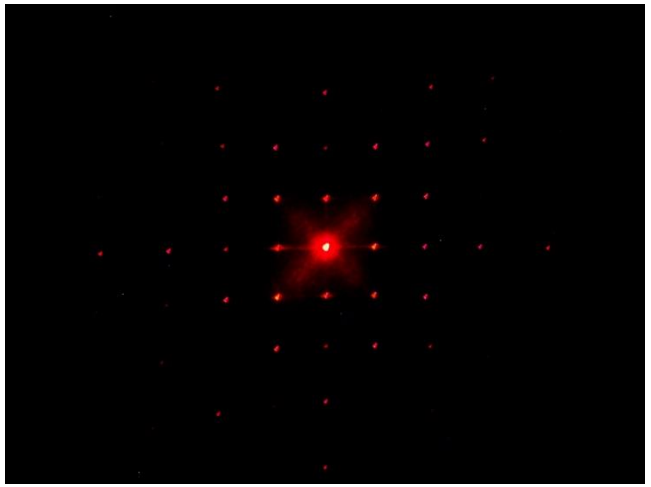
SEM photographs of micro columns

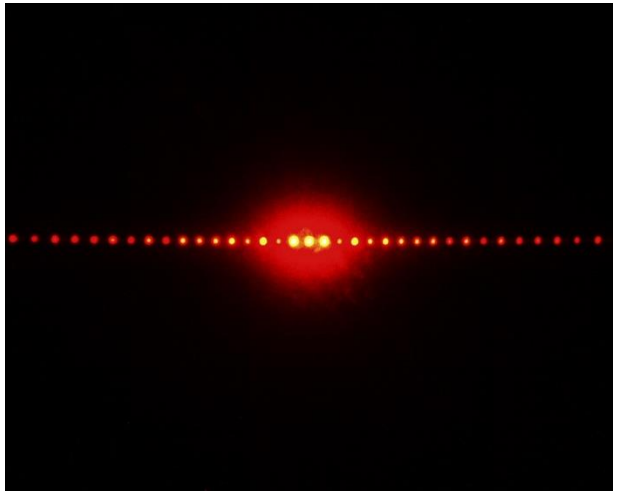
Replication of Micro-/Nano- structures

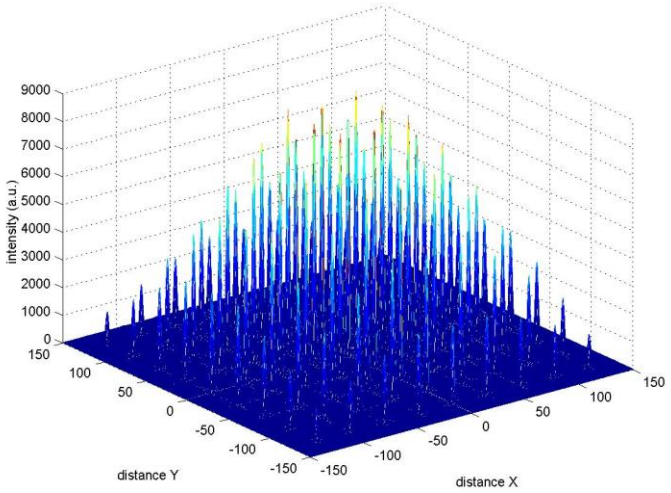


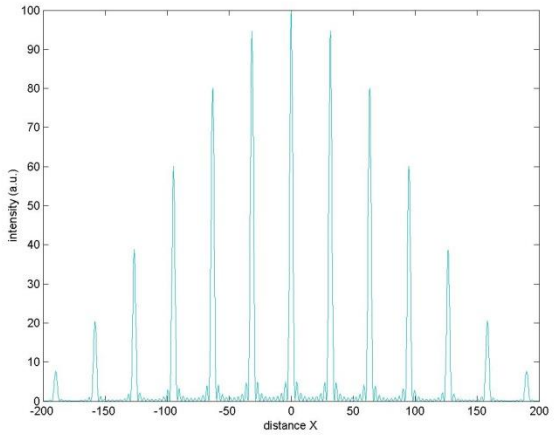
SEM photographs of gratings

Diffraction Pattern



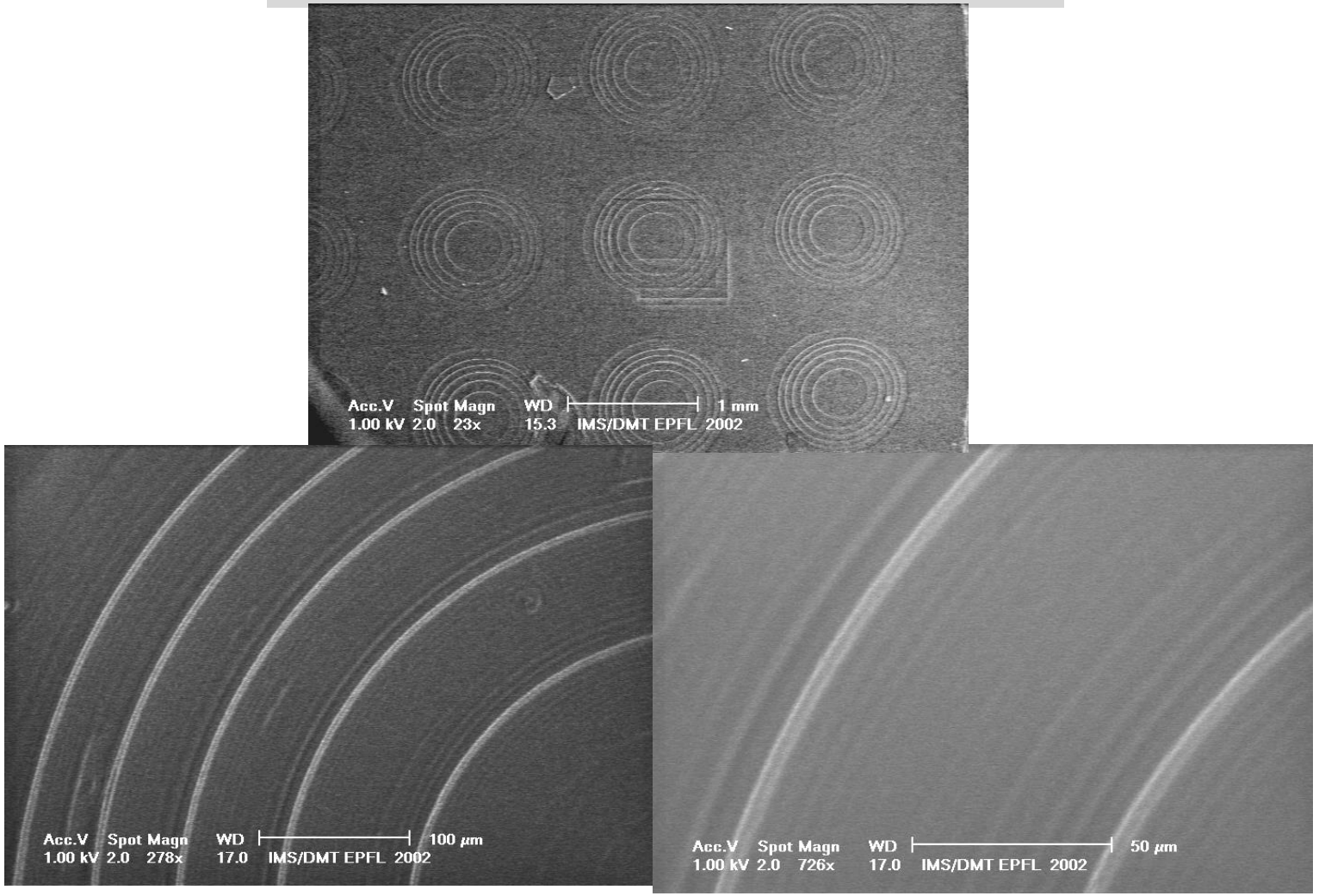






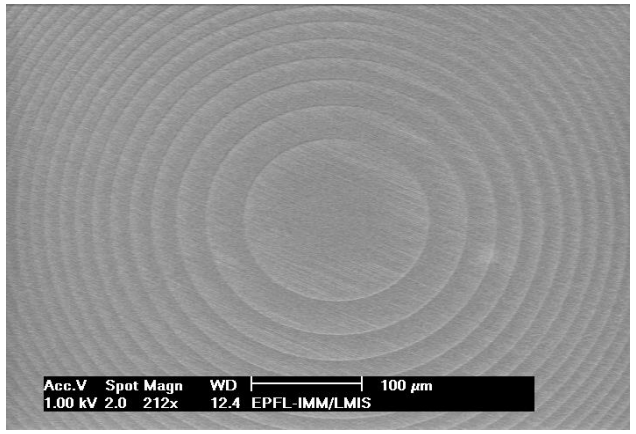
Replication of Micro-/Nano- structures

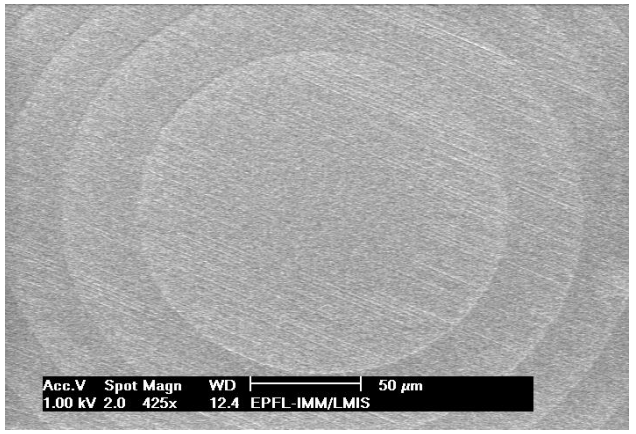
Replication of 3-D structure - fresnel lens

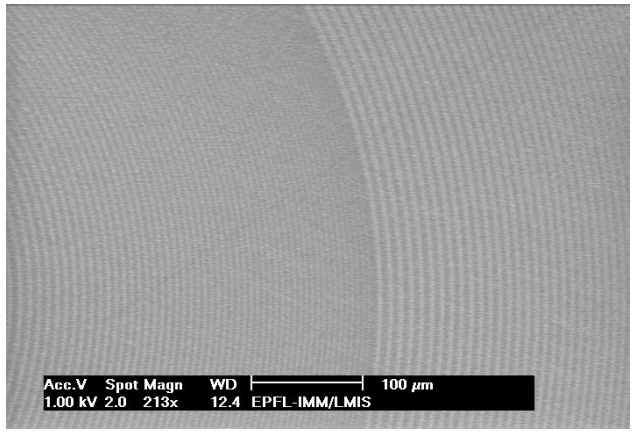


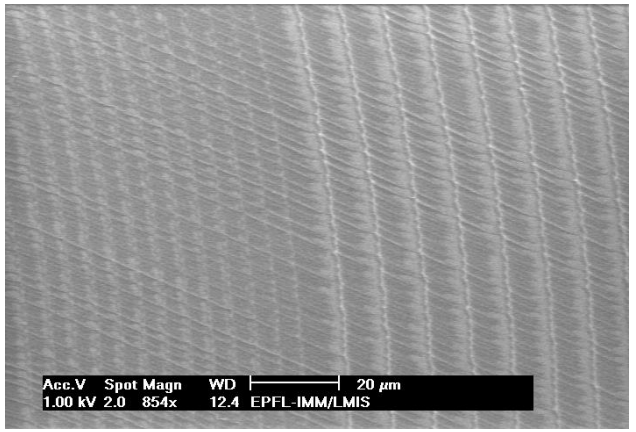
Replication of Micro-/Nano- structures

Replication of 3-D structure - fresnel lens



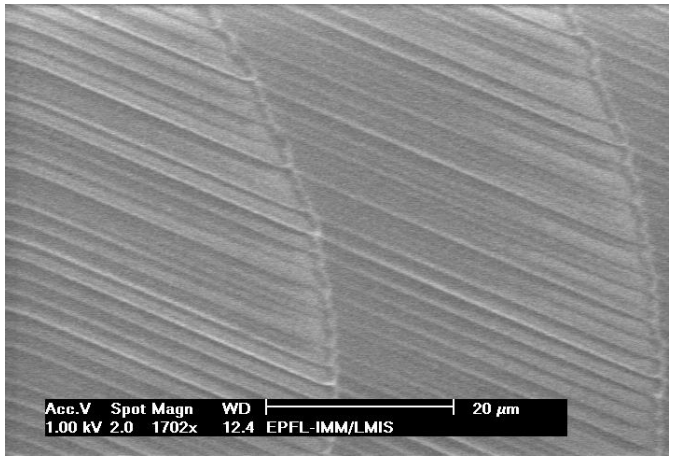


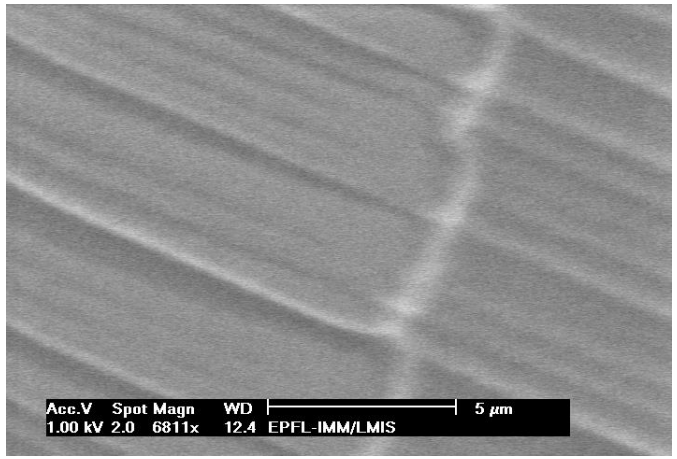


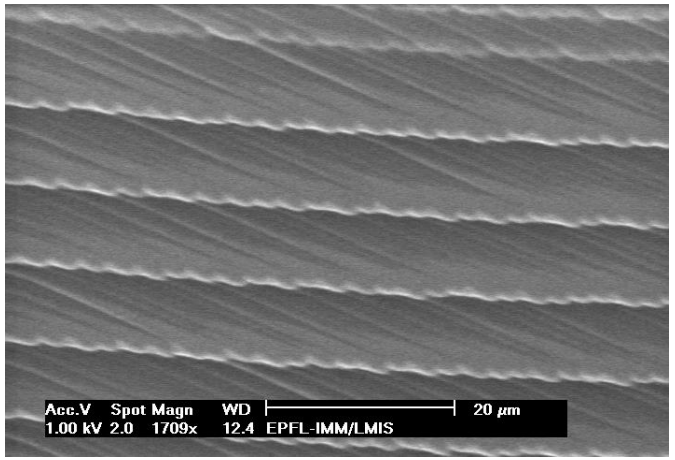


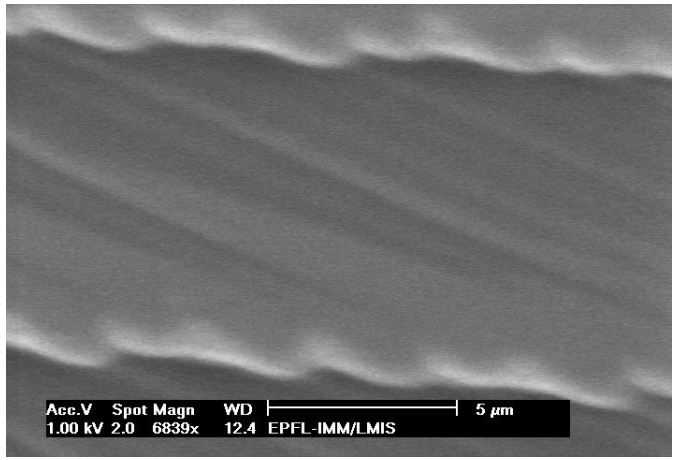
Replication of Micro-/Nano- structures

Replication of 3-D structure - fresnel lens

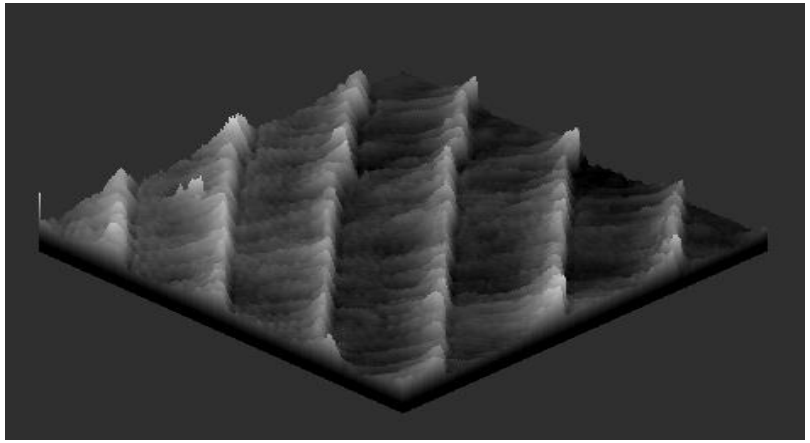


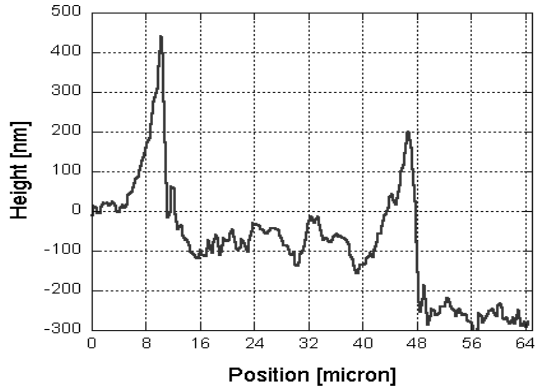




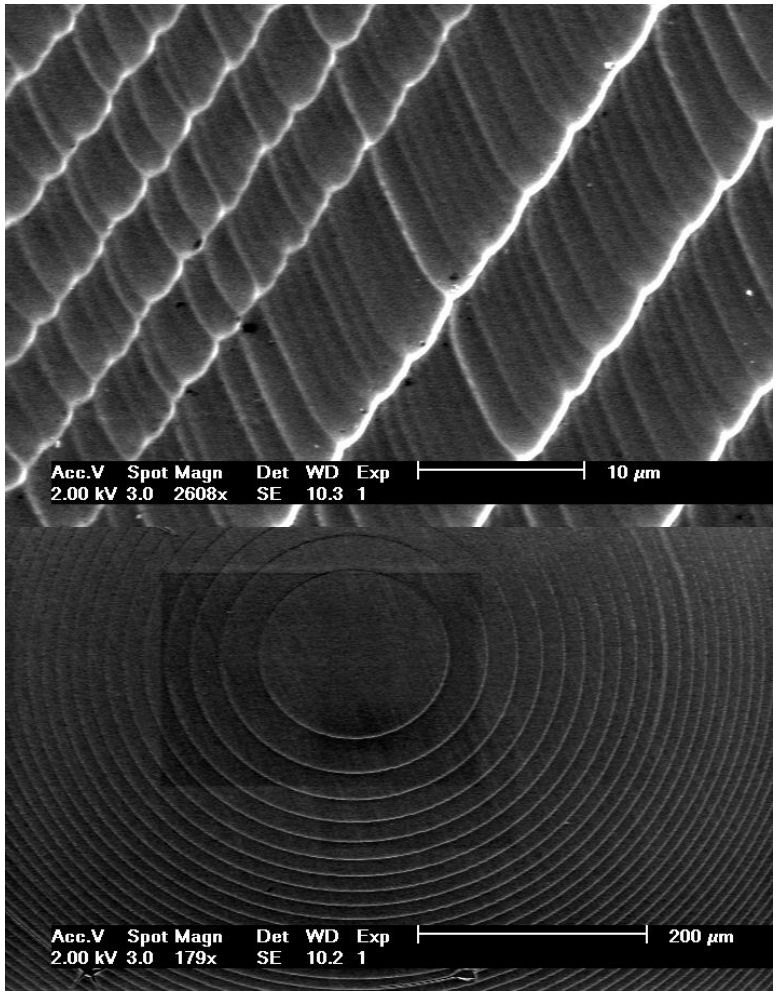


Replication of Micro-/Nano- structures in TiO_2

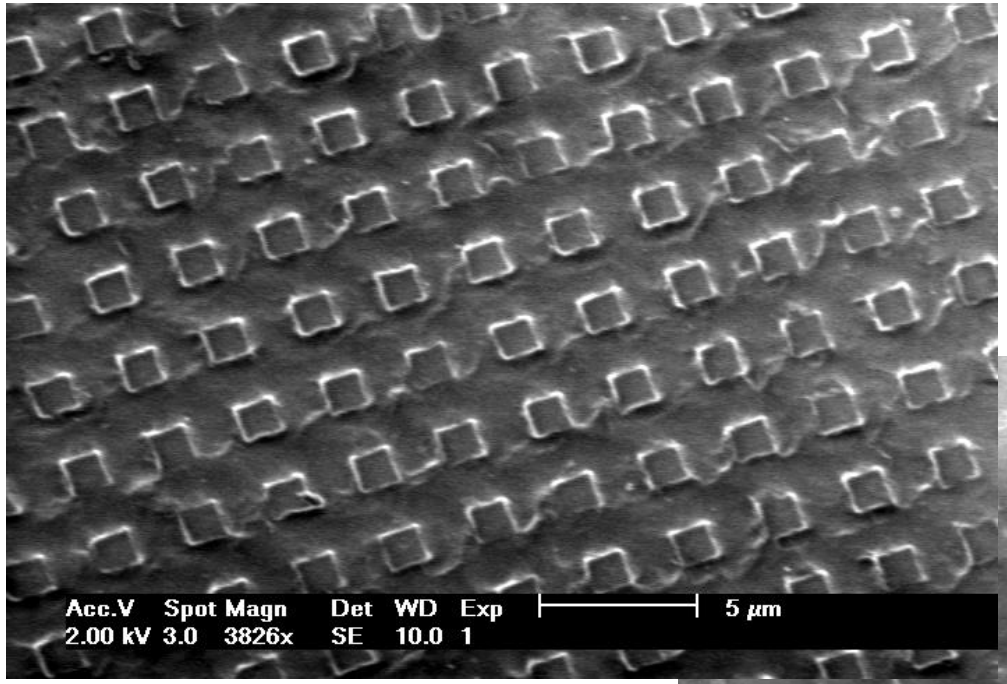


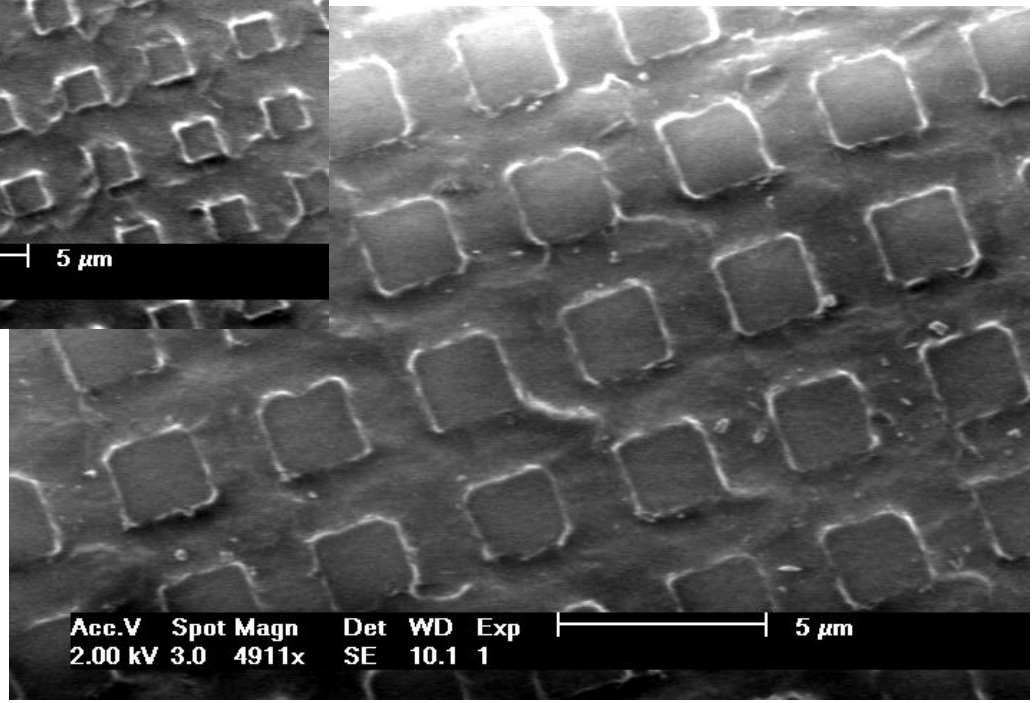


Profile of the TiO_2 DOE structures of the Fresnel lens, obtained by DHM (Digital Holographic Microscopy)



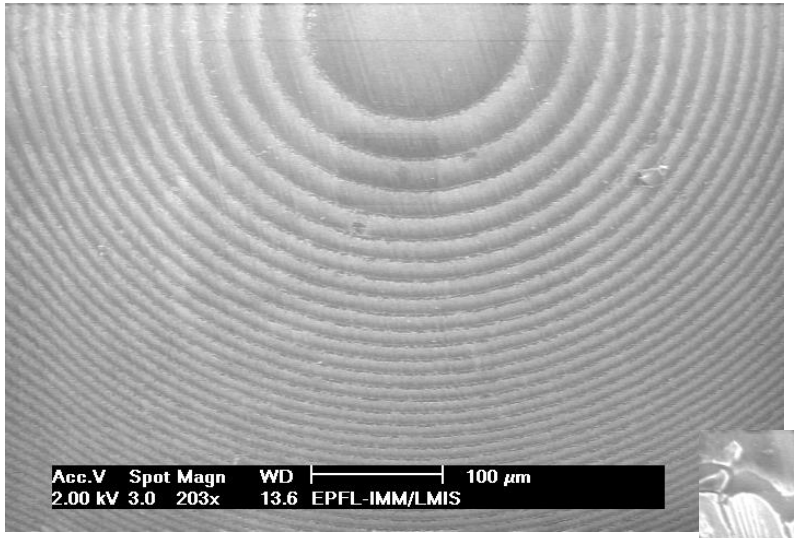
Replication of Micro-/Nano- structures in TiO_2

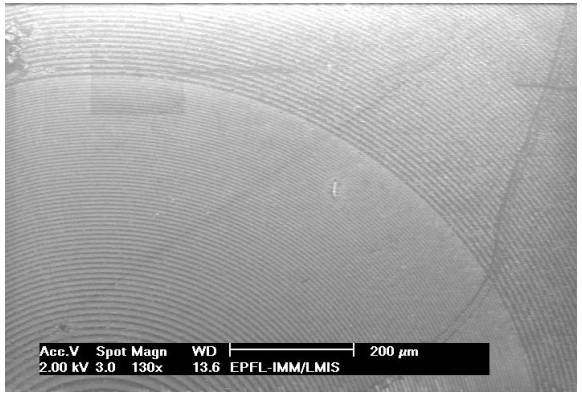


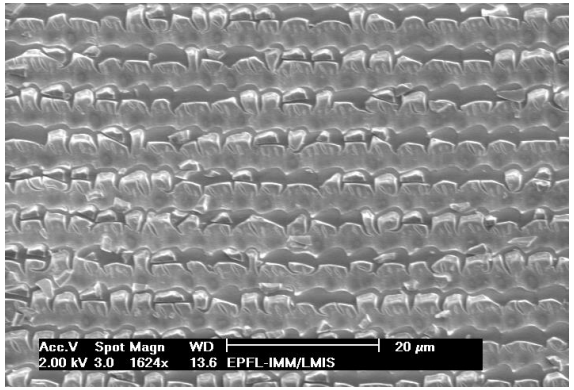


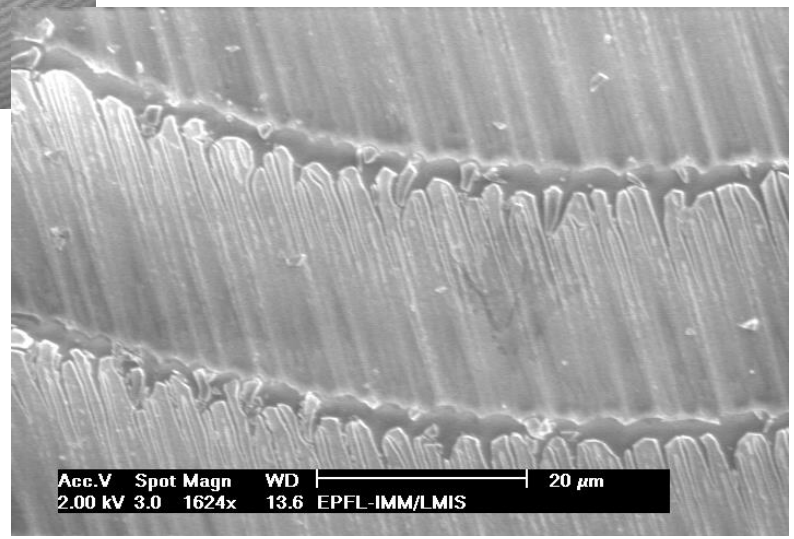
Replication of Micro-/Nano- structures

Replication of patterned glass coating (Effect of Thermal treatment)









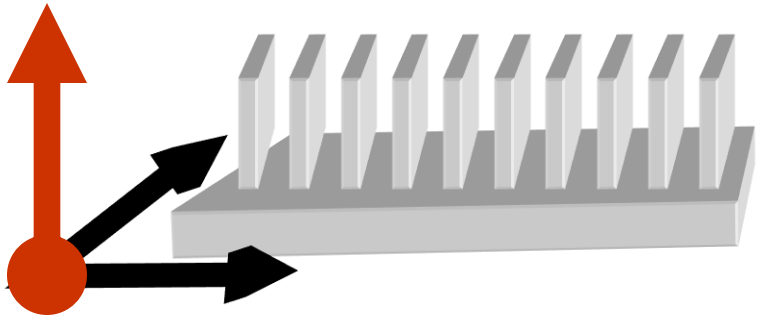
Shrinkage & Time consuming

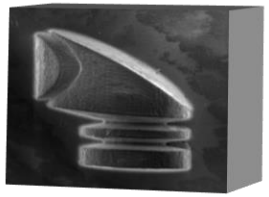
No shrinkage

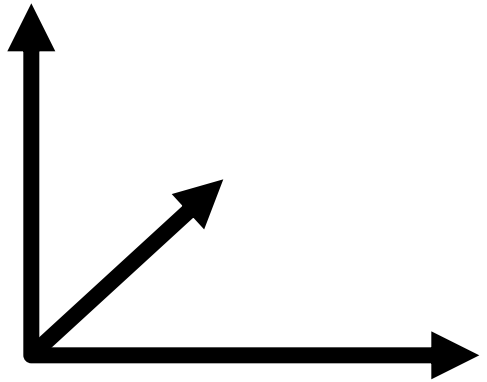
OR

Shrinkage Manipulation

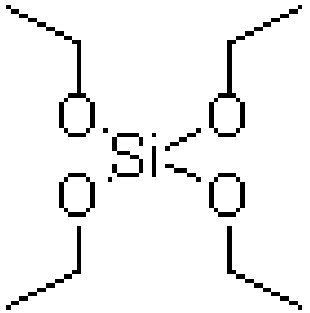
SHRINKAGE -- CONTROL / MANIPULATE



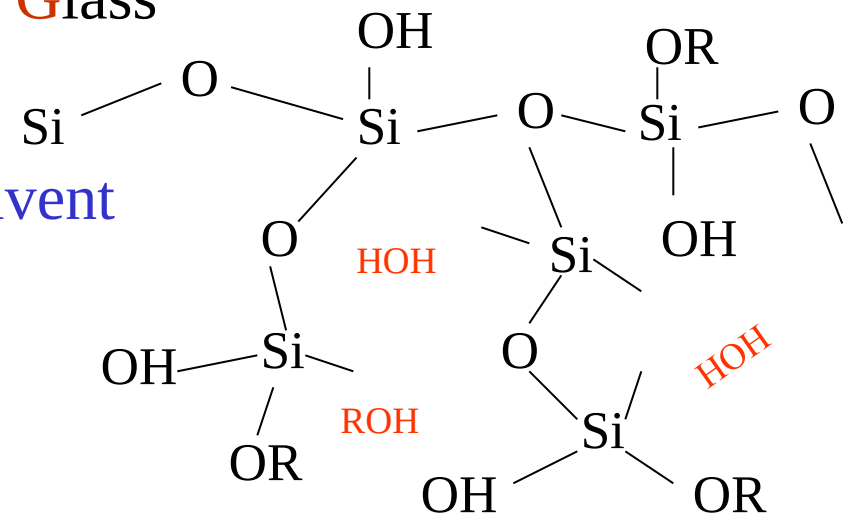


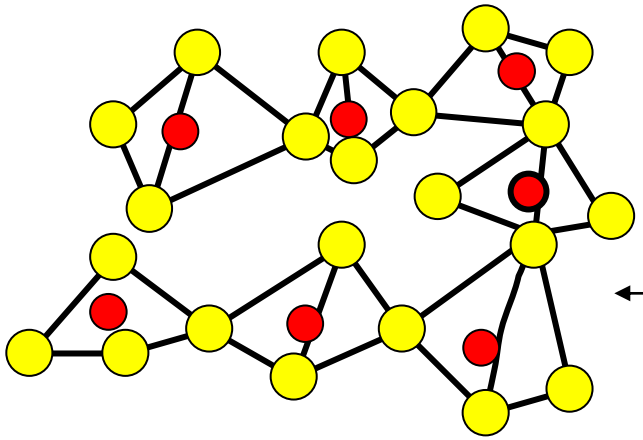


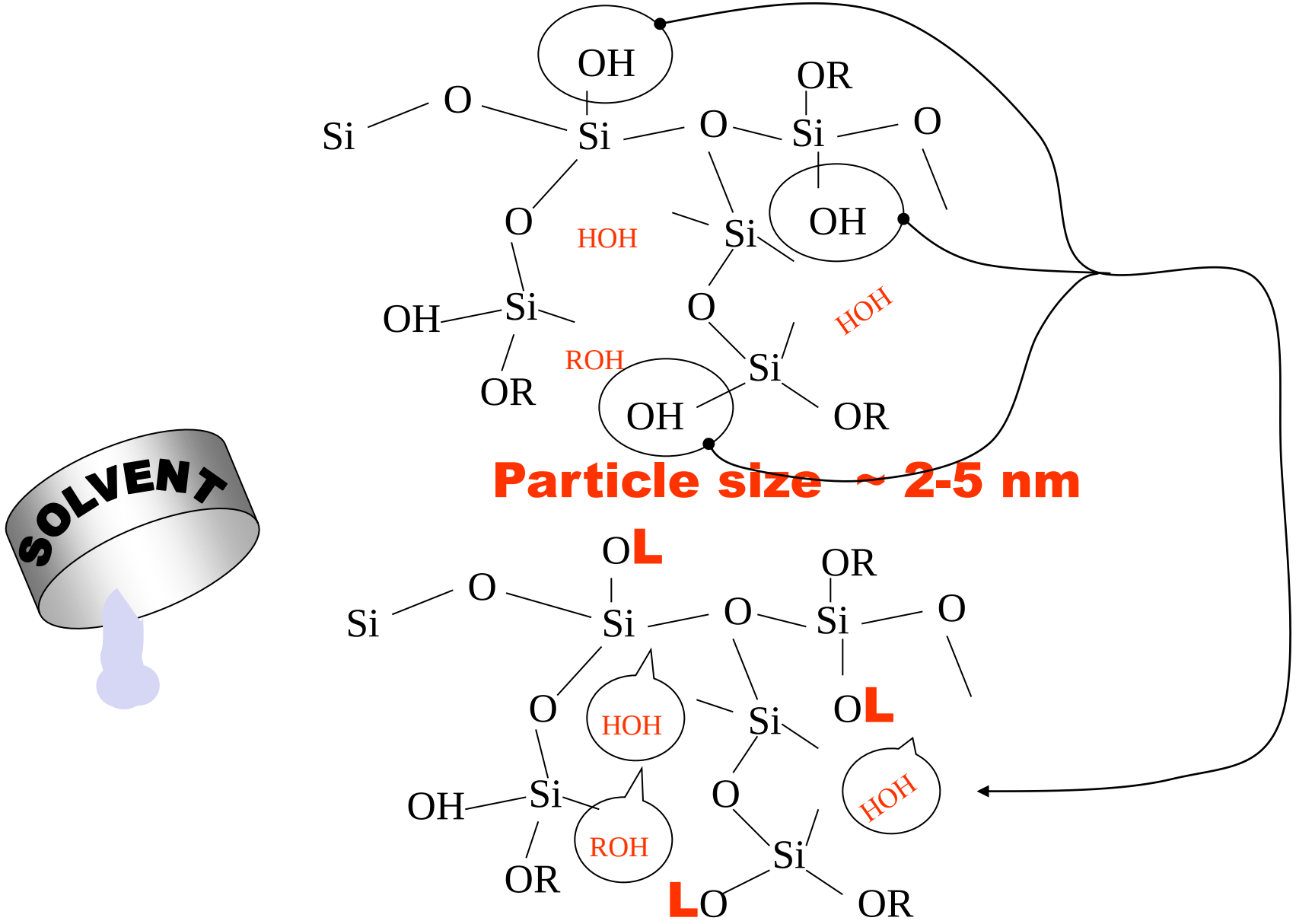
The Process – Sol Gel / Spin On Glass

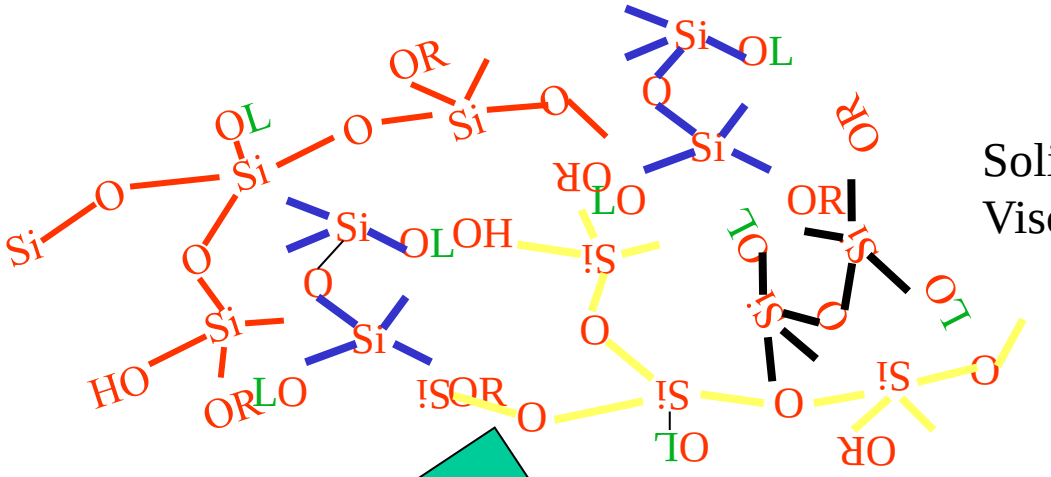


Catalyst/Water/Solvent





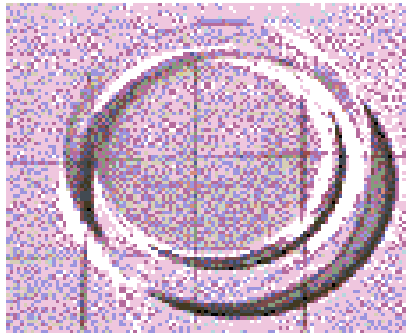

OH
OR
Si
O
HOH
ROH
SOLVENT
Particle size ~ 2-5 nm
L

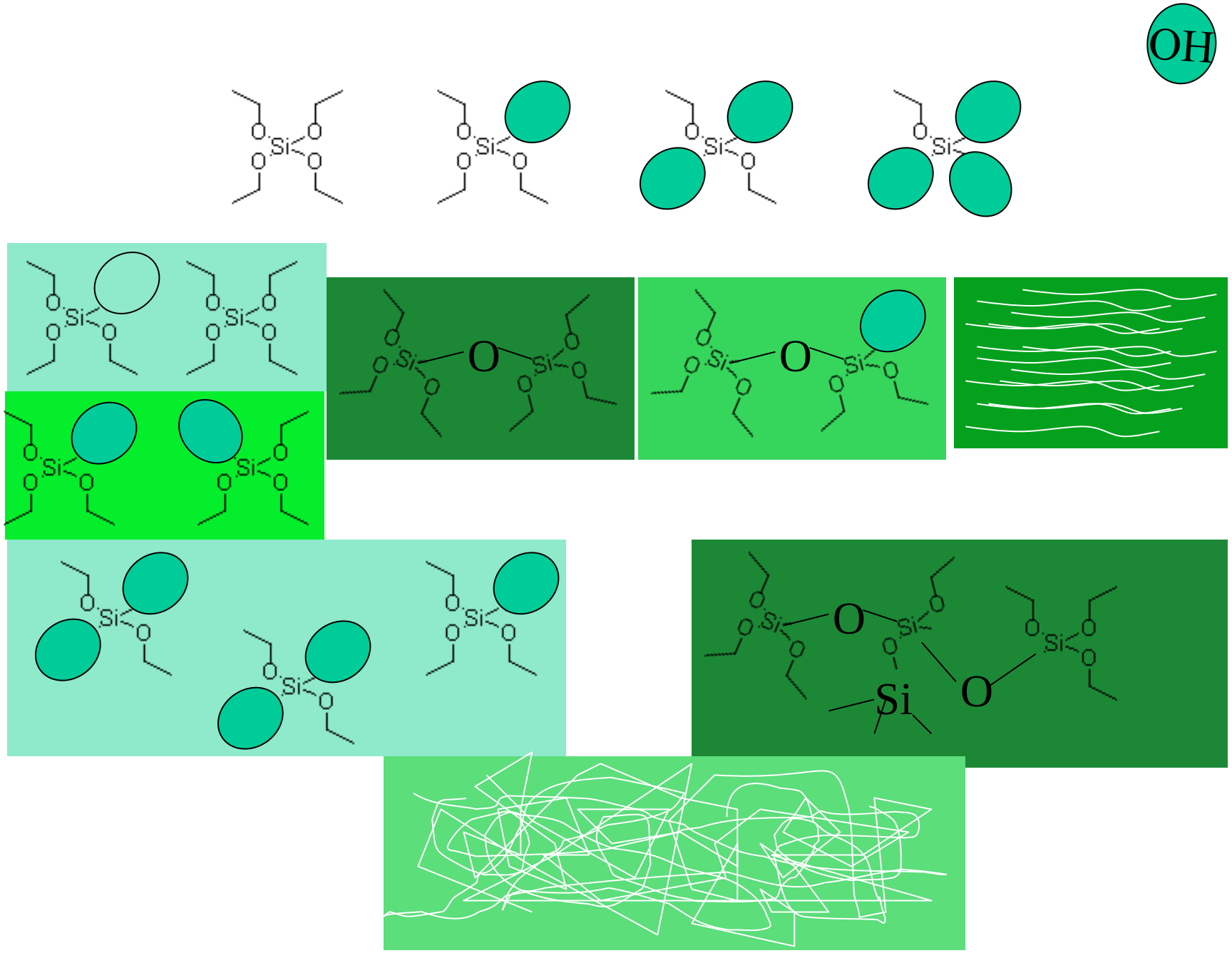


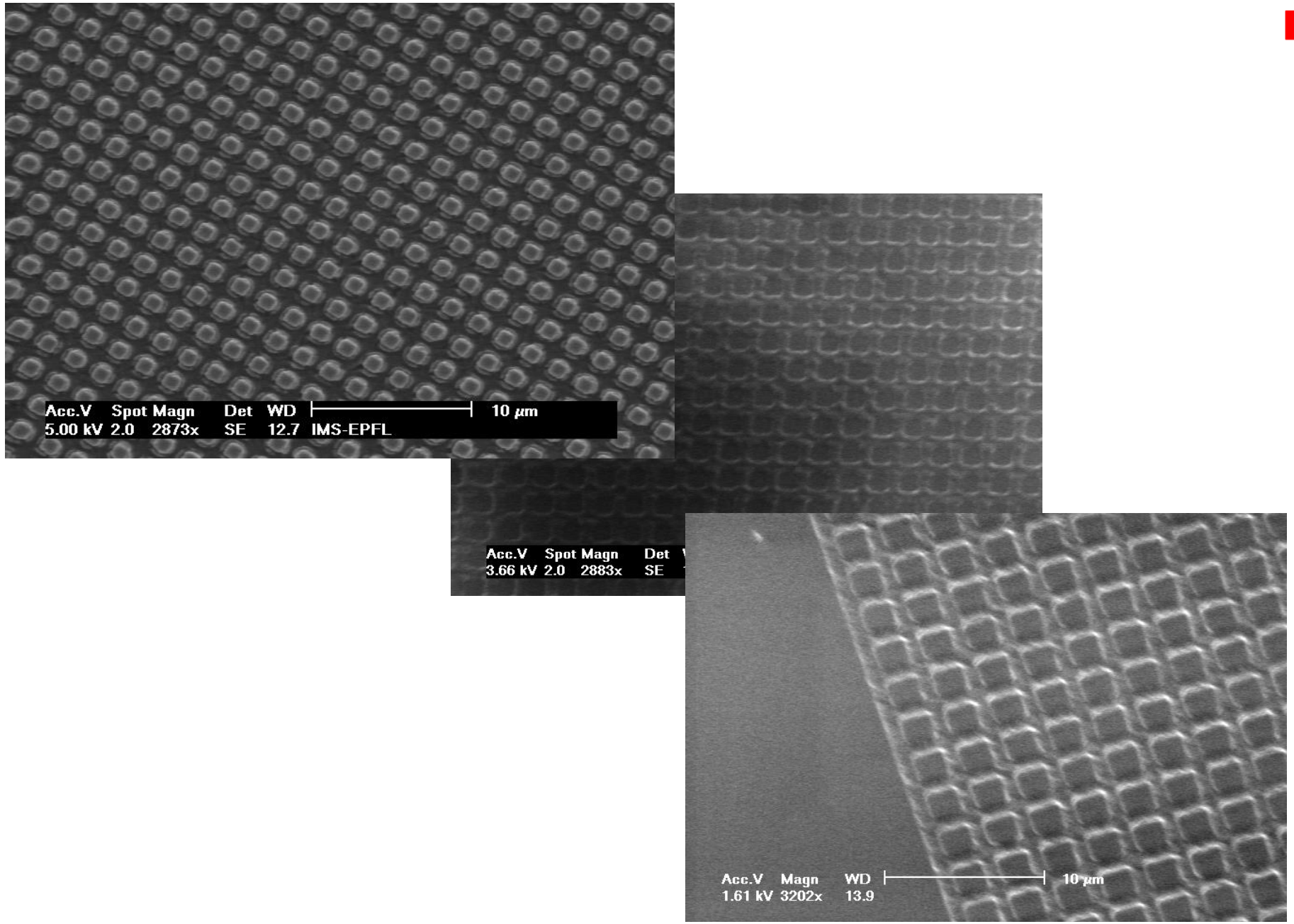
Solid Conc. ~ 65-67%
Viscosity = 10-12mPaS

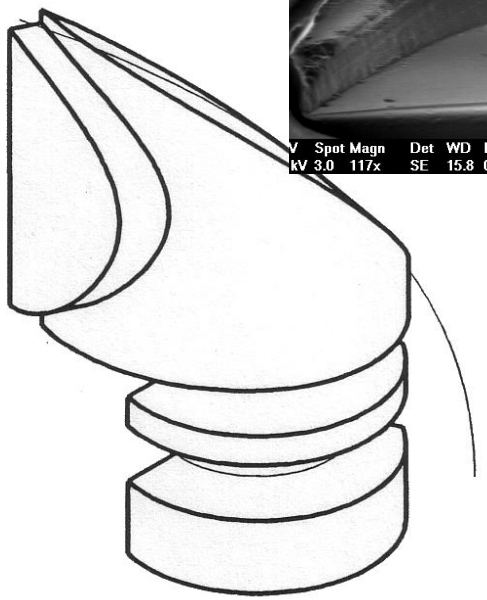
Catalyst
Lavelling Agent
Surface active agents
Adhesion promoter

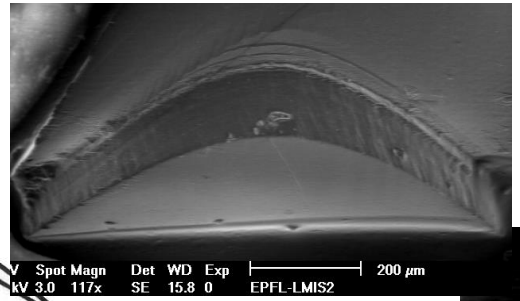
Reactive Oxide Solution

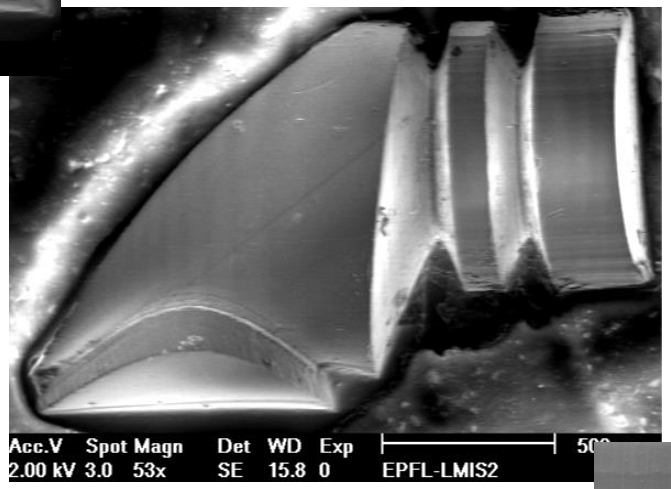


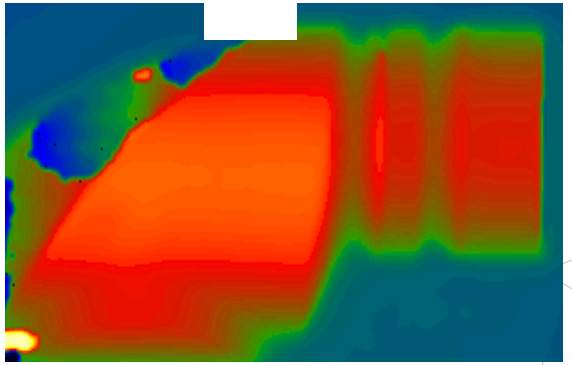

OH
Si
O

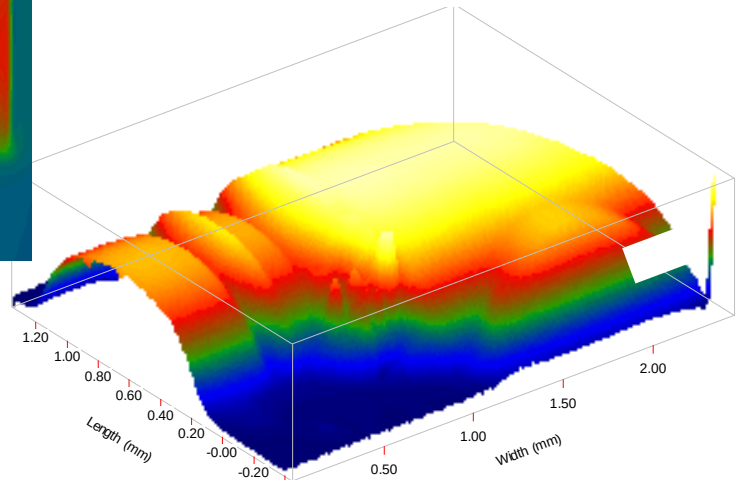

Acc.V Spot Magn Det WD 10 µm
5.00 kV 2.0 2873x SE 12.7 IMS-EPFL
Acc.V Spot Magn Det
3.66 kV 2.0 2883x SE
Acc.V Magn WD 10 µm
1.61 kV 3202x 13.9

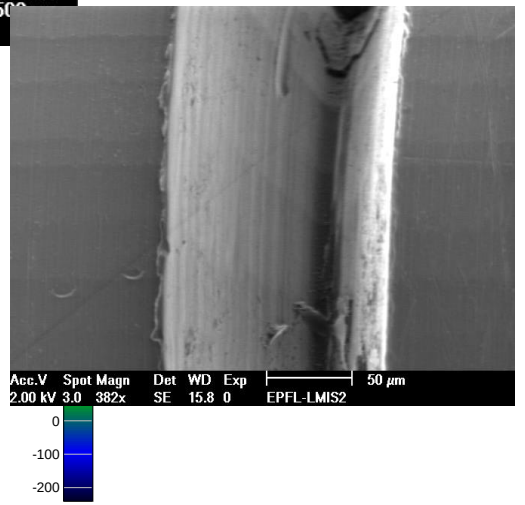



V Spot Magn Det WD Exp 200 µm
kV 3.0 117x SE 15.8 0 EPFL-LMIS2


Acc.V Spot Magn Det WD Exp
2.00 kV 3.0 53x SE 15.8 0 EPFL-LMIS2

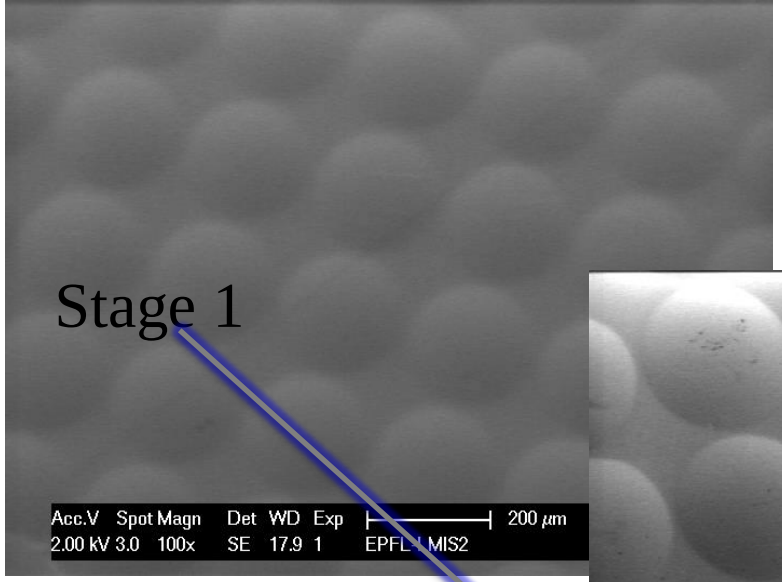


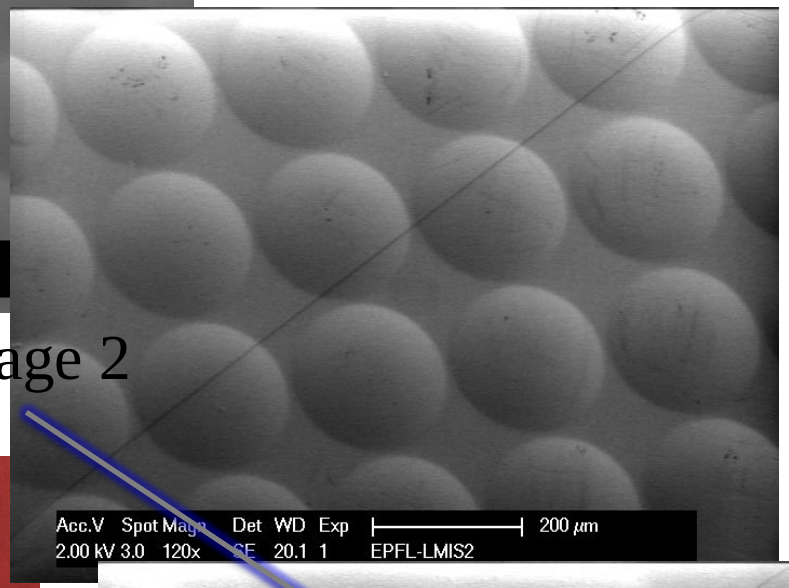

1.20
1.00
0.80
0.60
0.40
0.20
-0.00
-0.20
Length (mm)
0.50
1.00
1.50
2.00
Width (mm)

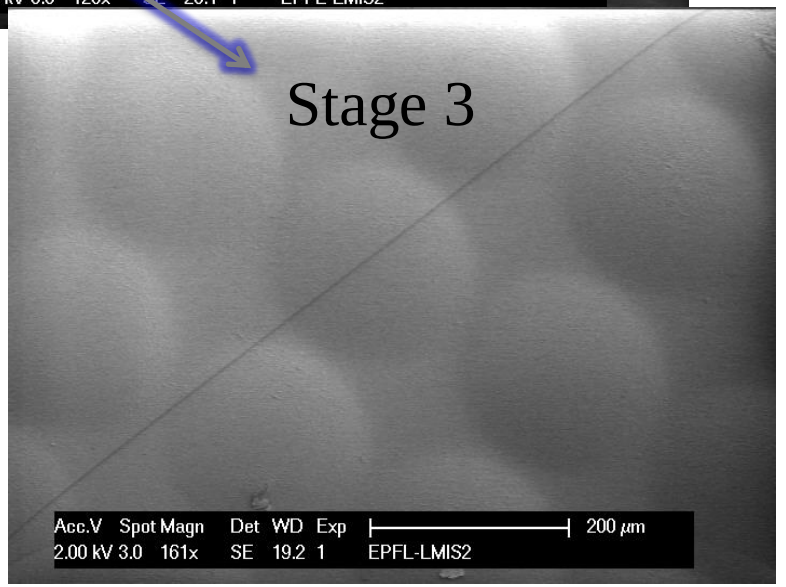

Acc.V Spot Magn Det WD Exp 50 µm
2.00 kV 3.0 382x SE 15.8 0 EPFL-LMIS2
0
-100
-200

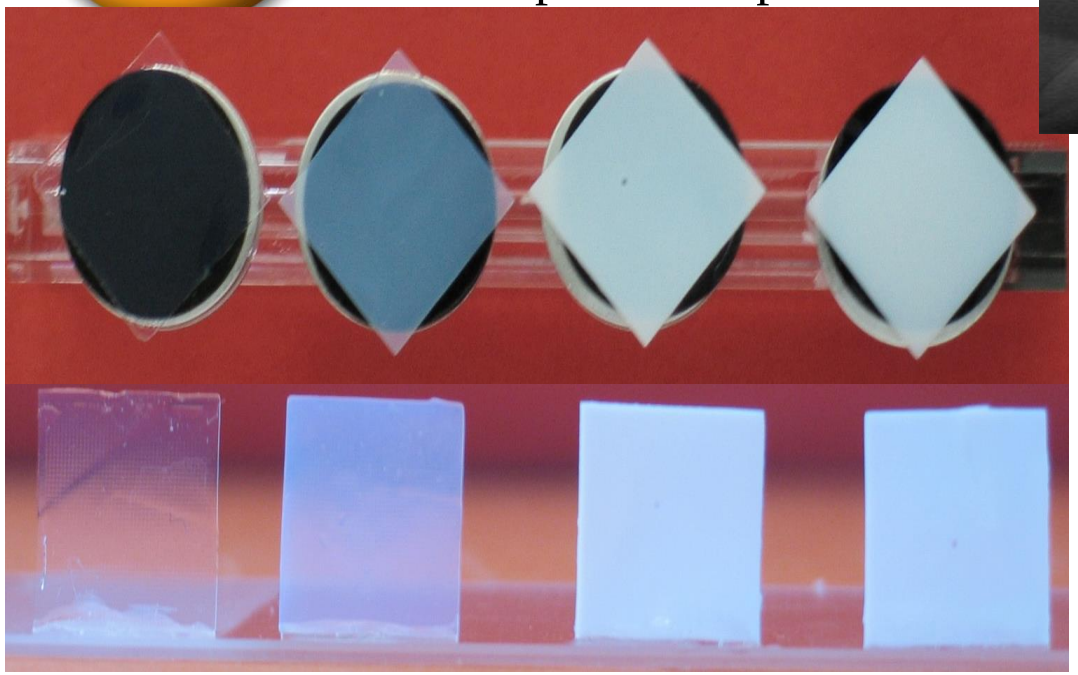
Shrinkage free fast route

Not for optical components



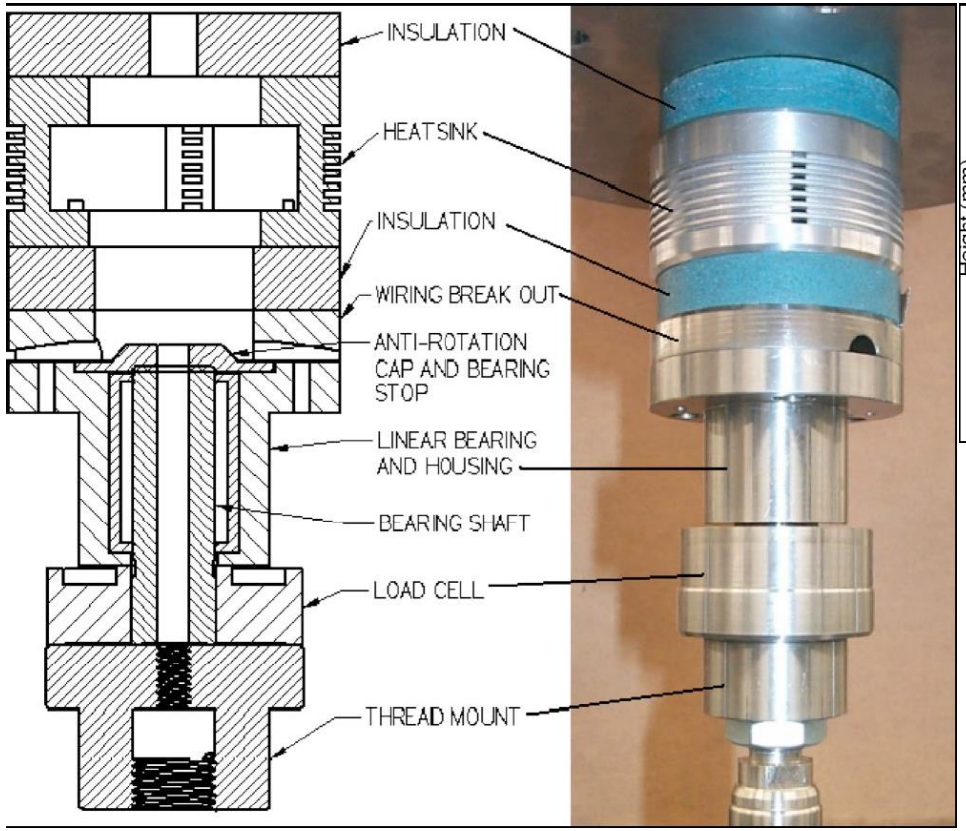




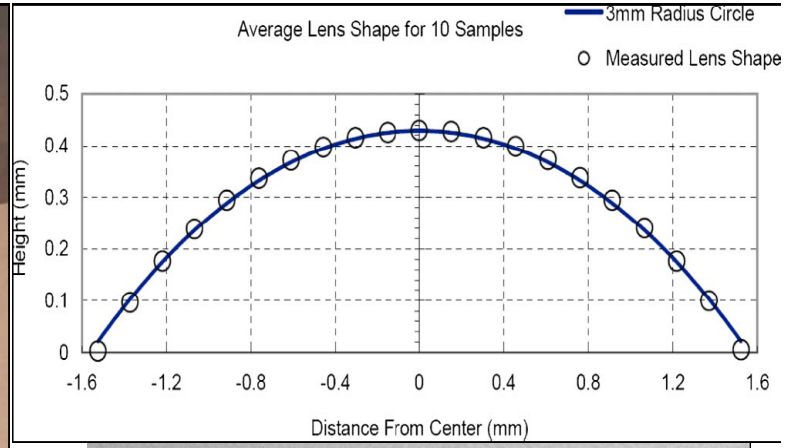


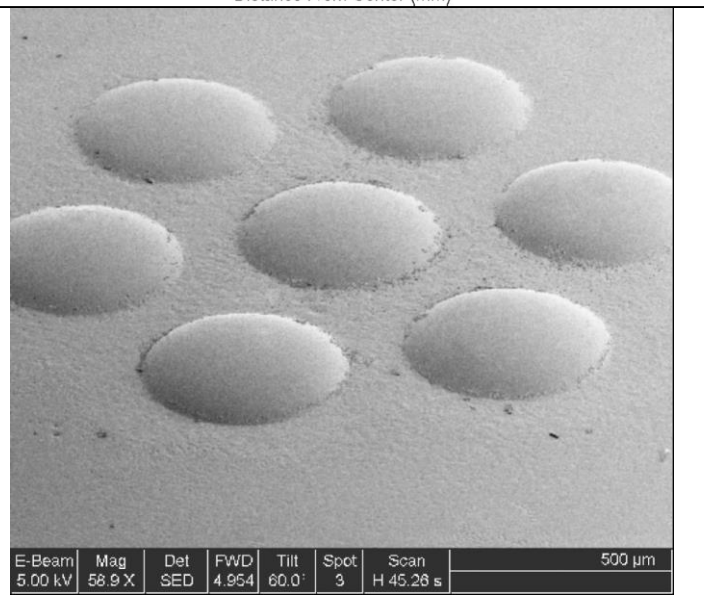
High temperature compression molding of glass

(The Ohio State University, Anurag Jain)



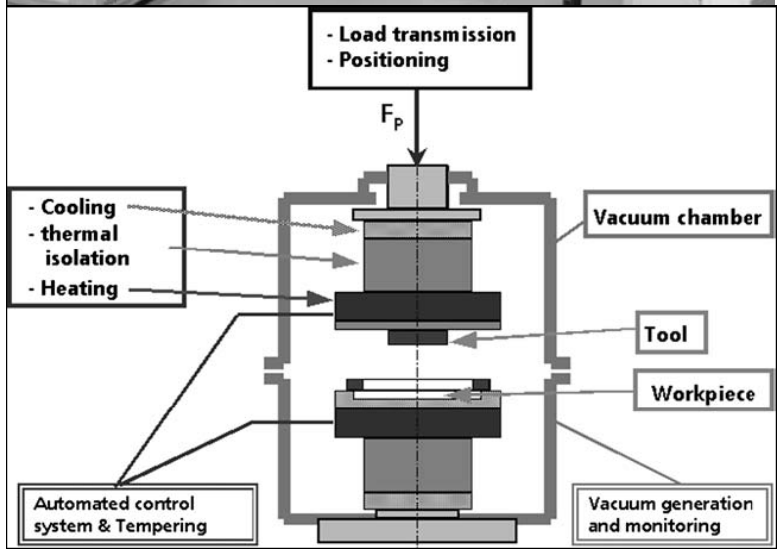
Load Cell

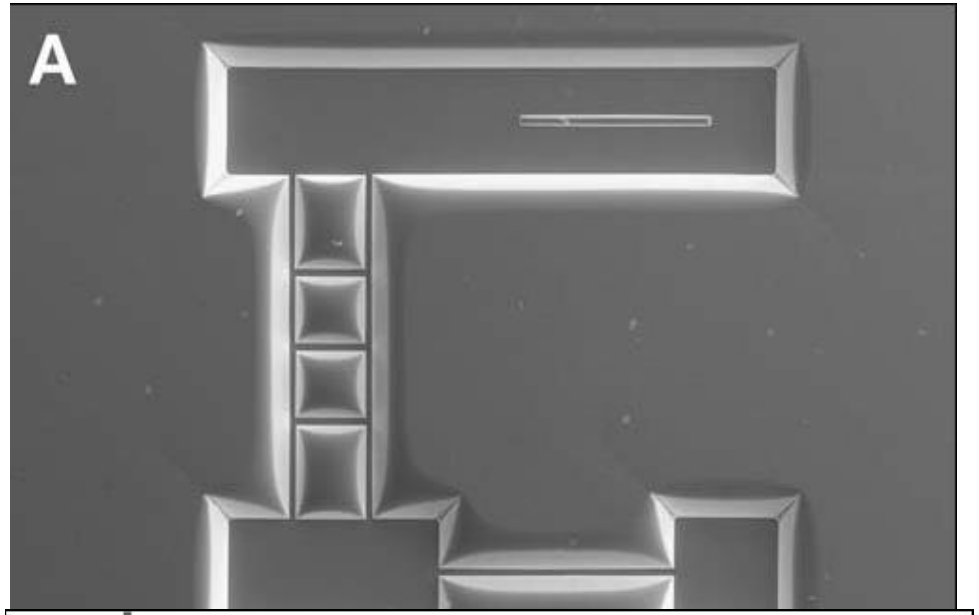


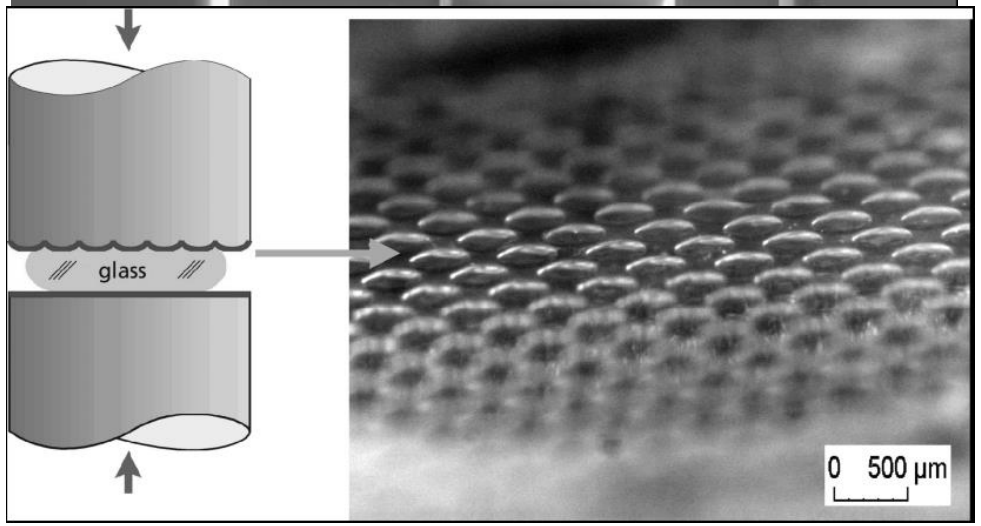


High-temperature micro-forming of Glass

Edelmann Fraunhofer Institute for Machine Tools and Forming Technology IWU, Germany

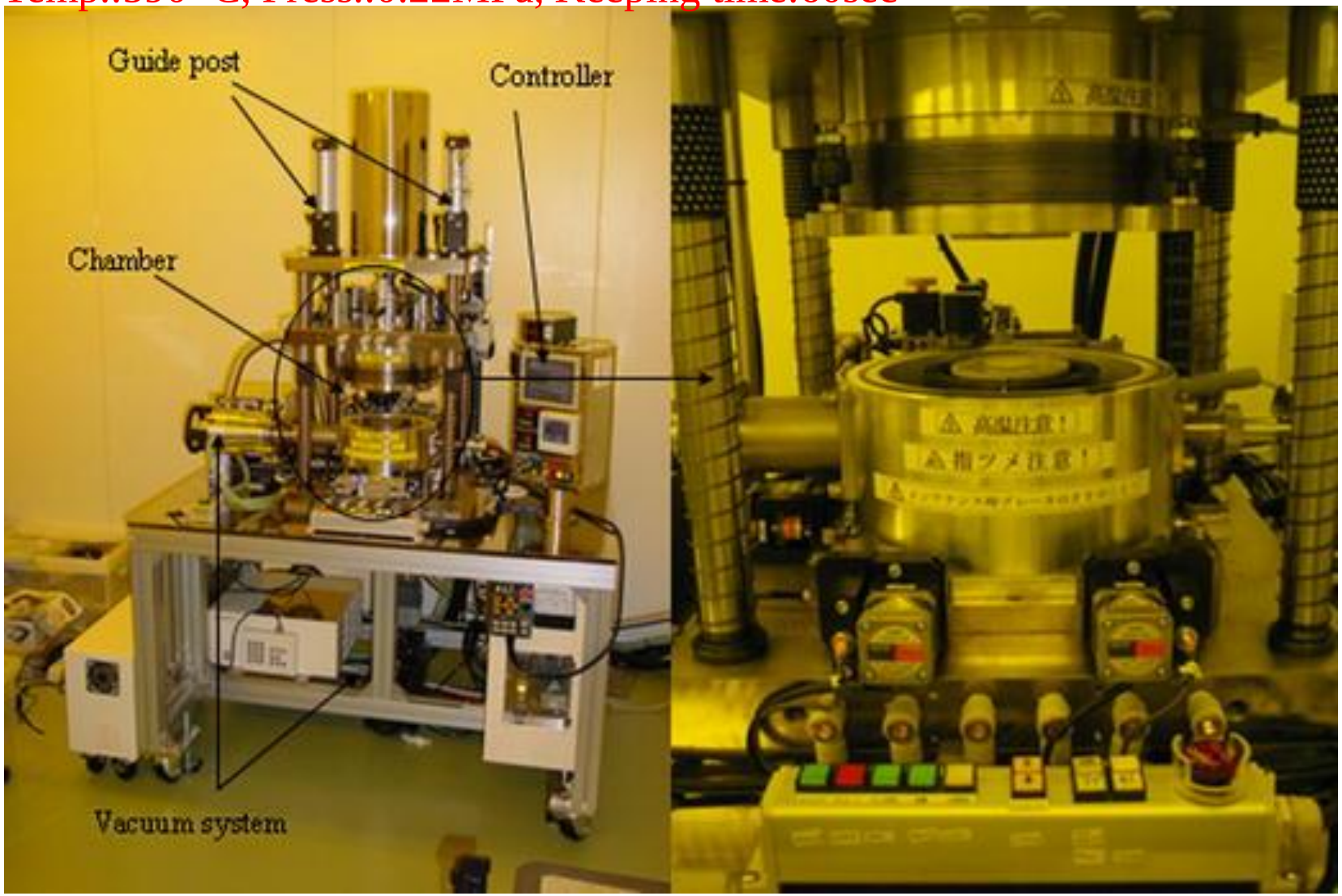


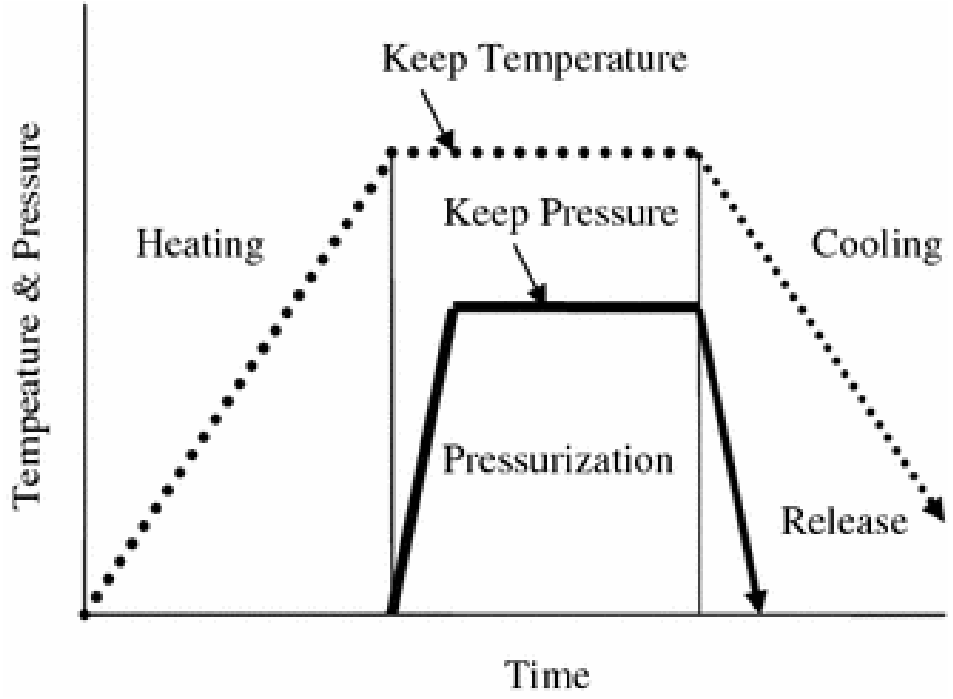


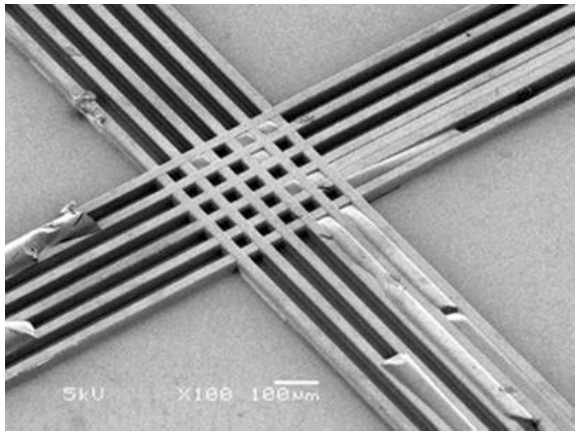


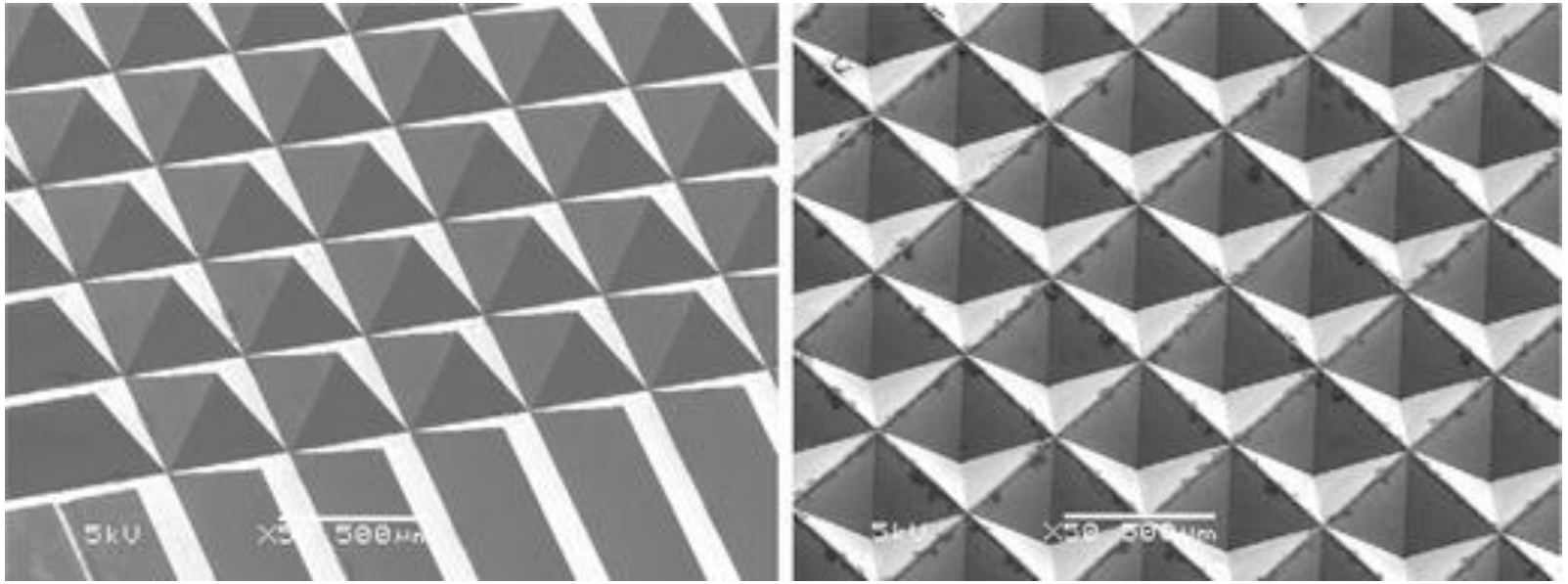
Hot Embossing Pyrex Glass with Glassy Carbon Mold fabricated by Focused-Ion –Beam Etching (AIST)

Temp.:590 ºC, Press.:0.22MPa, Keeping time:60sec

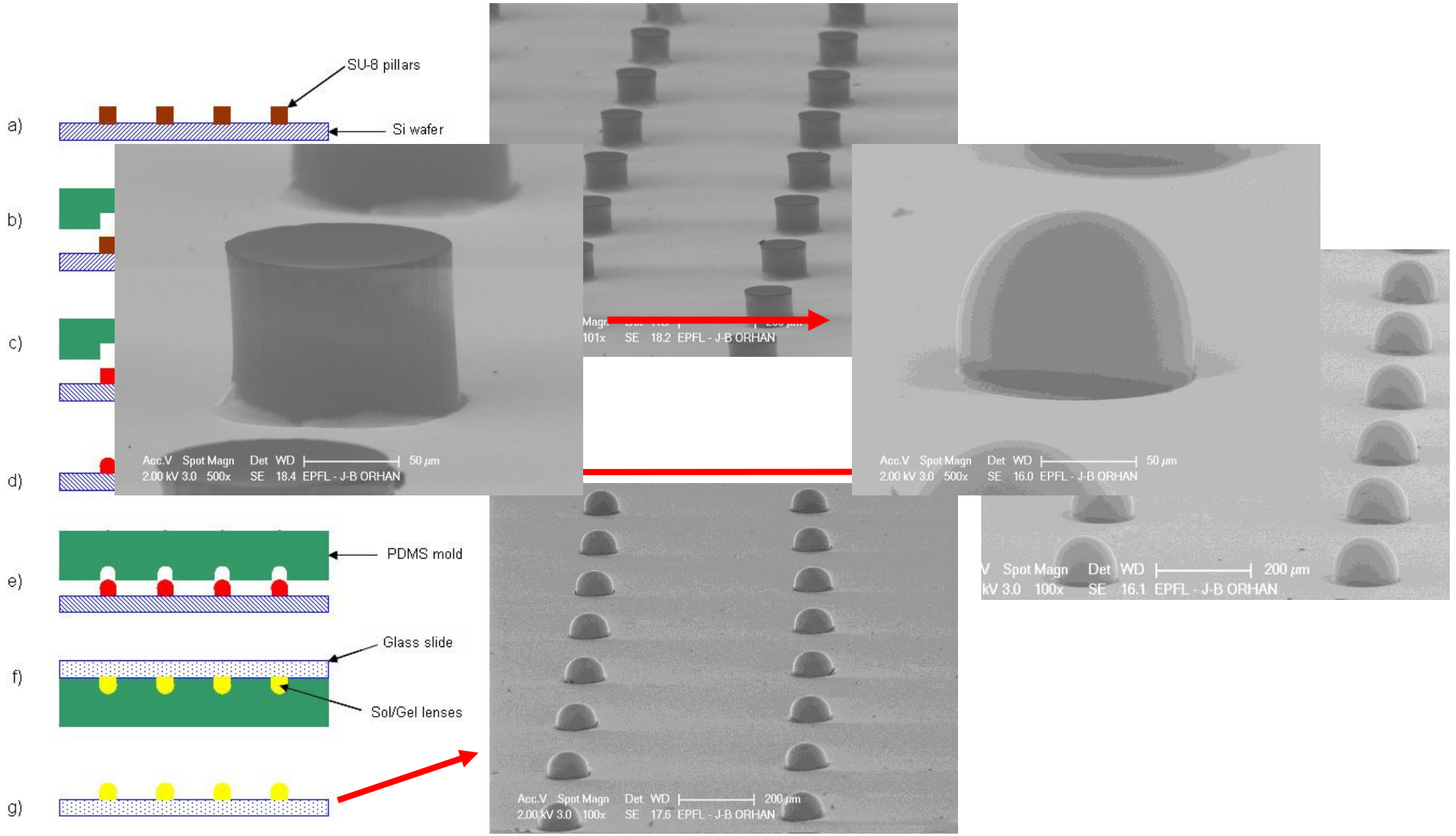



Keep Temperature
Heating
Keep Pressure
Cooling
Tempeature & Pressure
Pressurization
Release
Time


5kU X100 100µm


5kU

Fabrication of three-dimensional micro-lens arrays



Hybrid organic-inorganic glasses

inorganic chemistry = organic chemistry

room temperature

metal-organic precursors in organic solvents

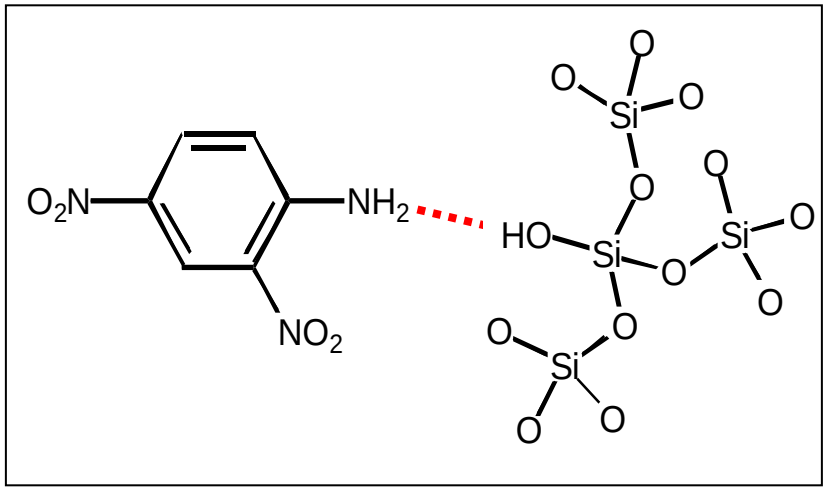
a whole range of new materials from brittle glasses to plastic polymers

Hybrid organic-inorganic materials

Classification

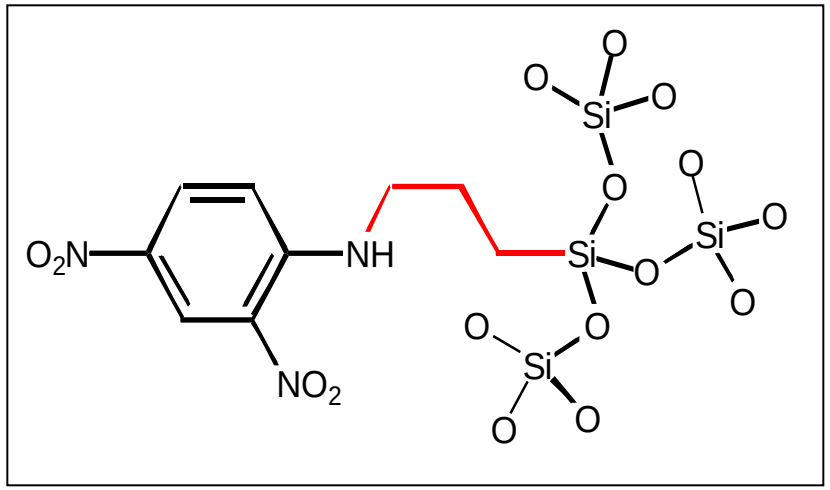
based on the nature of interactions between organic and inorganic components

Class I
No chemical bond between components
only weak interactions
(van der Waals, hydrogen, electrostatic)



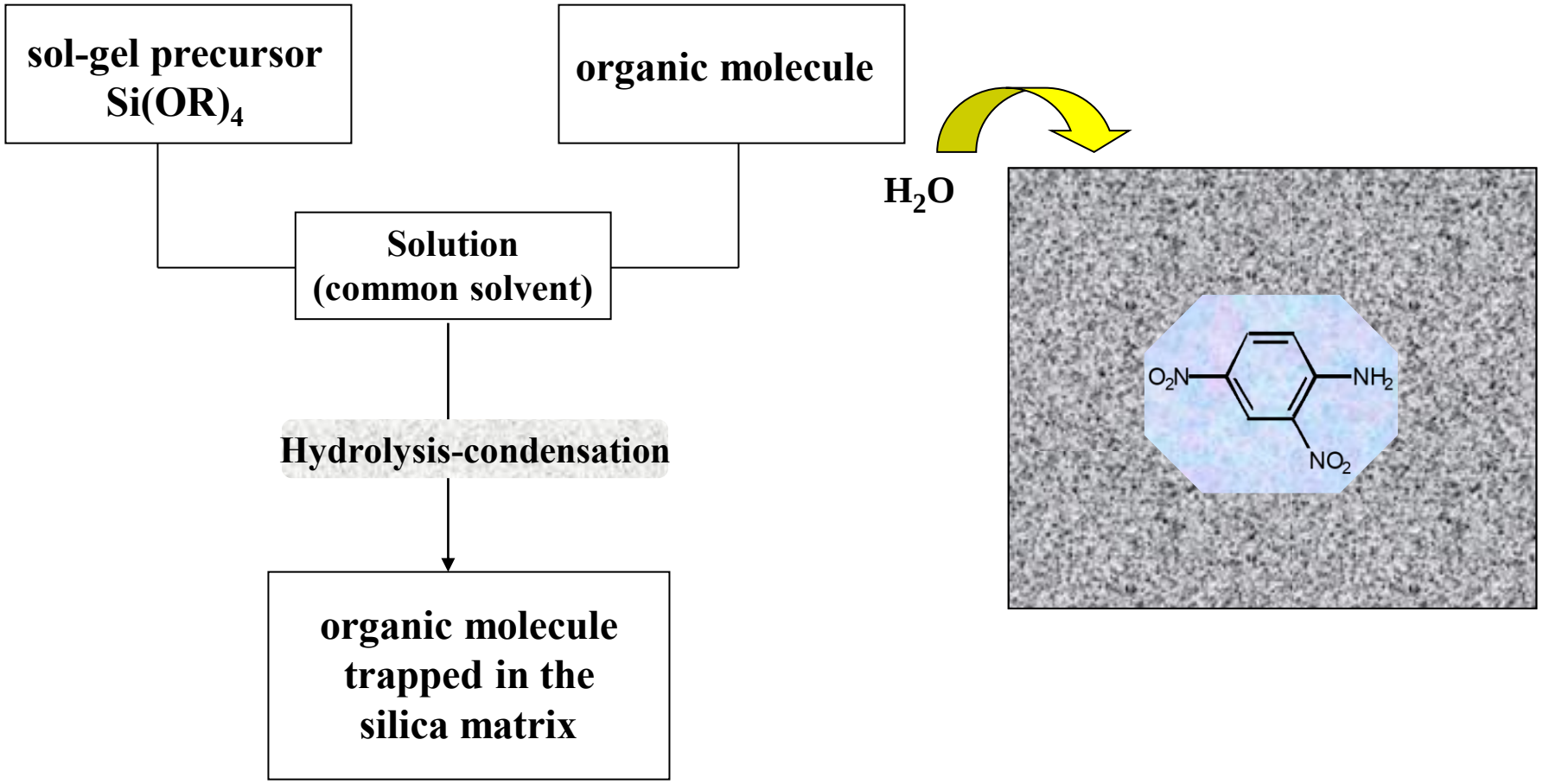
Entrapping

Class II
Chemical bonds between components
strong interactions
(covalent bonds)

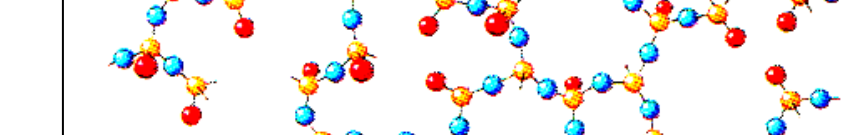


Grafting

Class I
the organic molecule is trapped within the silica network



Class II : network modifier



Si-O-Si network + pending organic groups

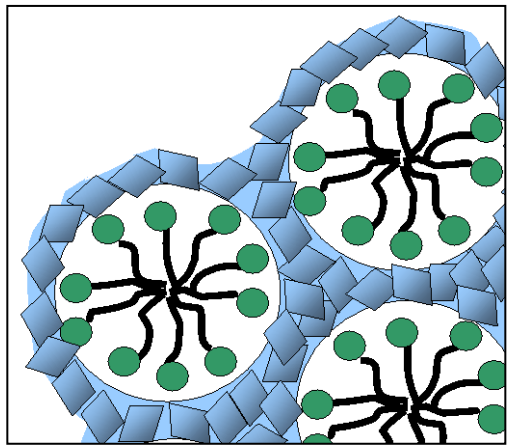
Si-O-Si chains + side organic groups

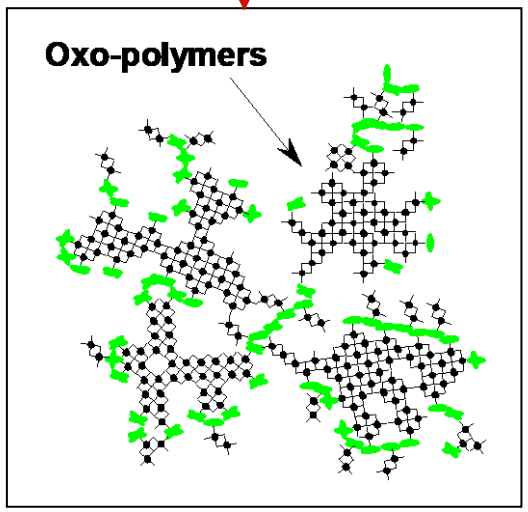
Synthesis of hybrid organic-inorganic materials

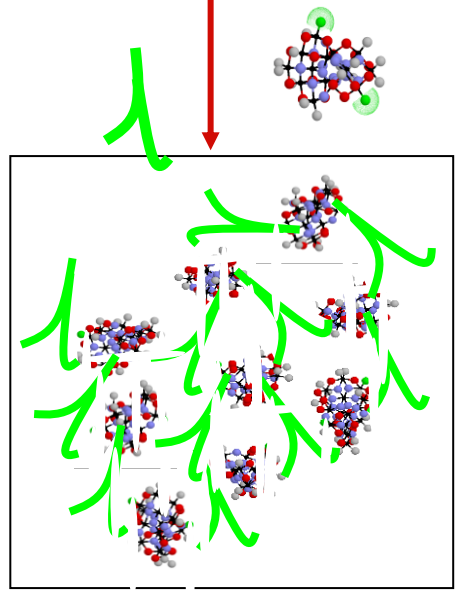
$$R\text{-}Si\text{-}(OR)_x + M(OR)_n$$

organo-functional alkoxide | metal alkoxide

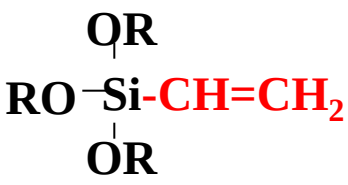
organic templates — conventional sol-gel route — inorganic building blocks



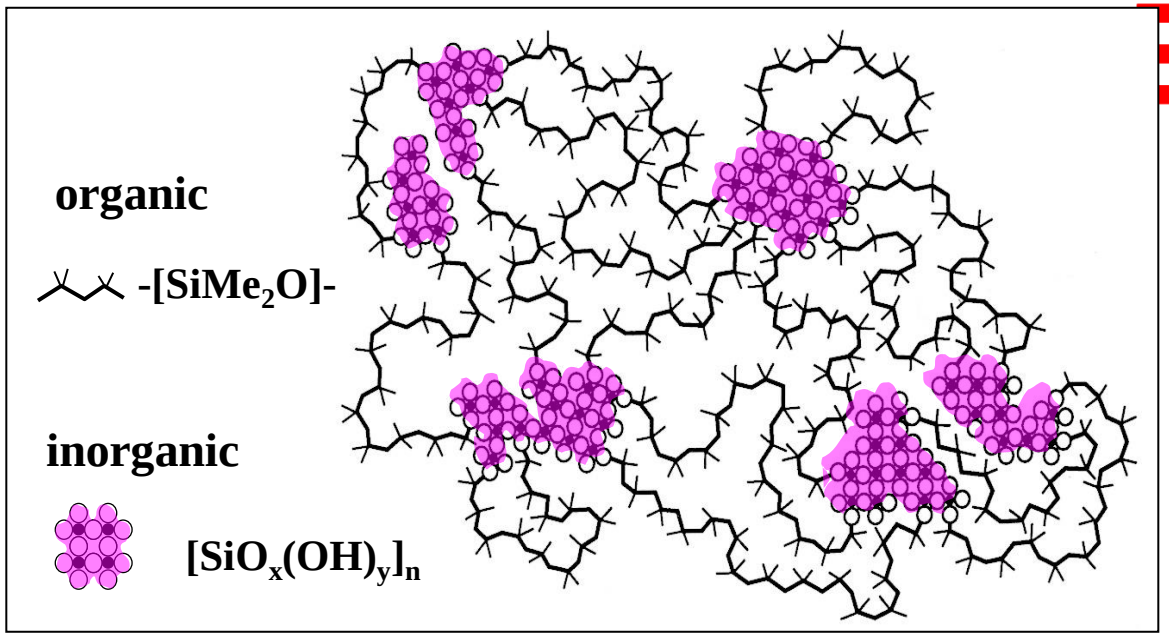




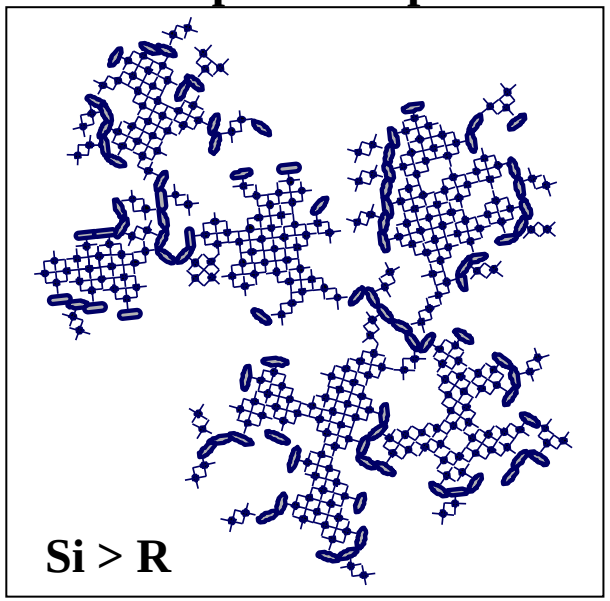
Class II : network formers

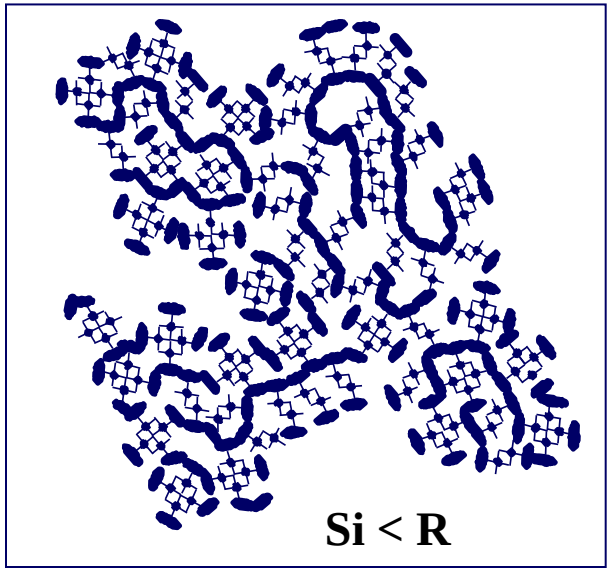


Double polymerization process



The size of both phases depends on the Si/R ratio






aerogel
xerogel

ORMOSIL

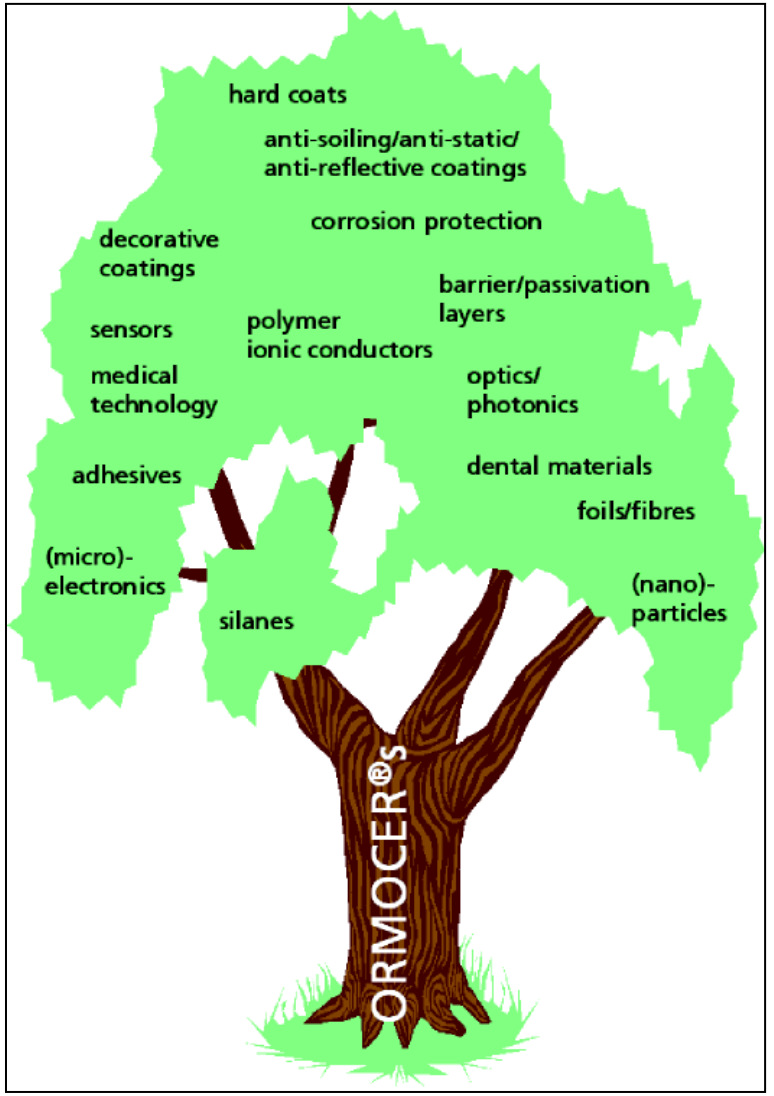
ORganically MOdified SILicate

ORMOCER

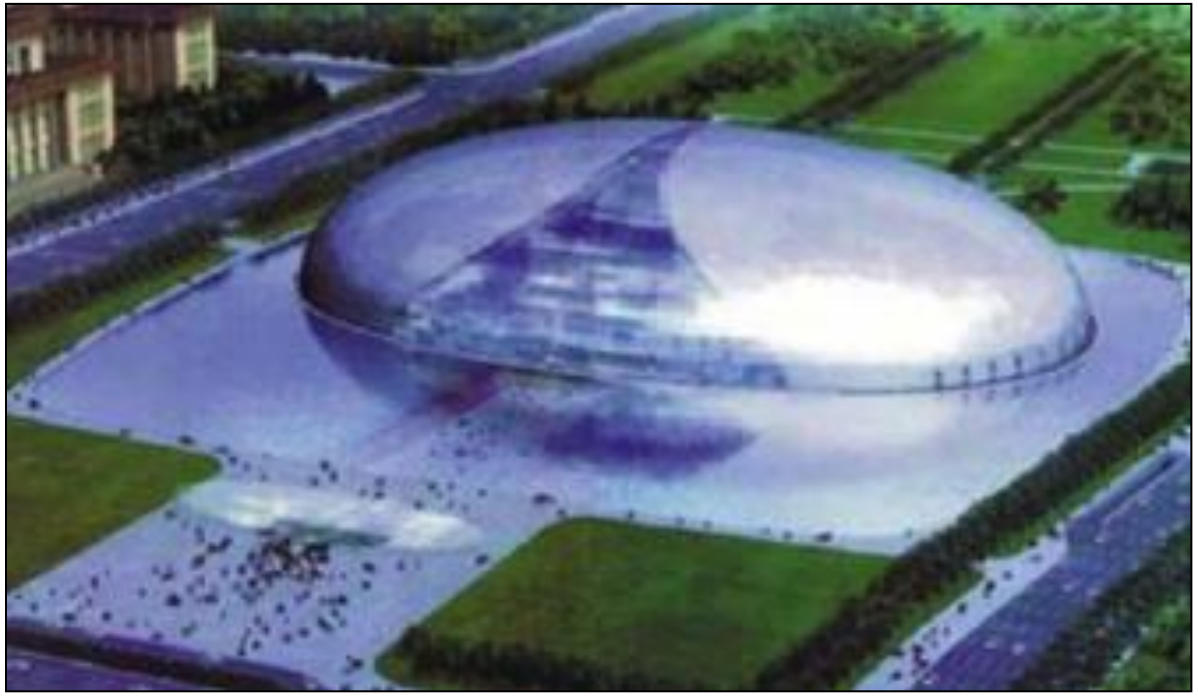
ORganically MOdified CERamic

CERAMER

CERAmic polyMER



Hybrid Sol-Gel Coatings



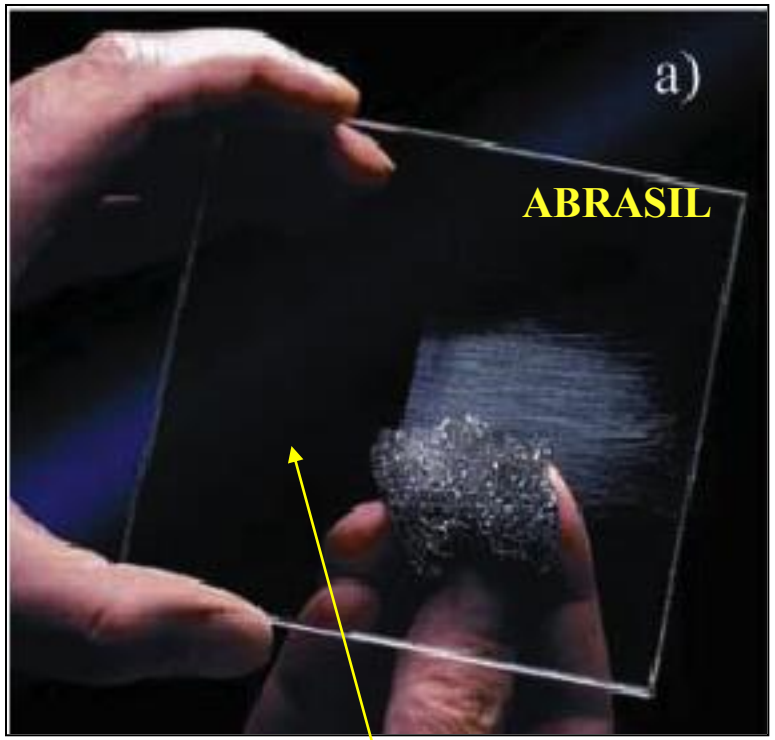
Le dôme du

grand théâtre national chinois

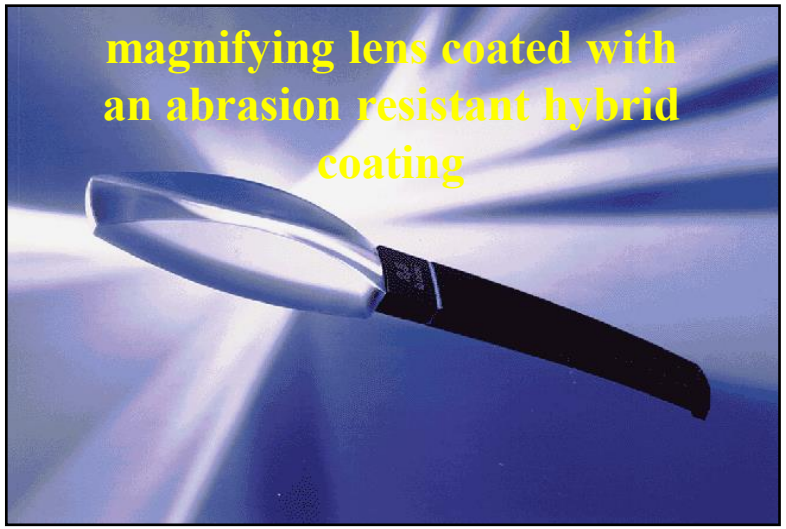
est recouvert d'un revêtement auto-nettoyant

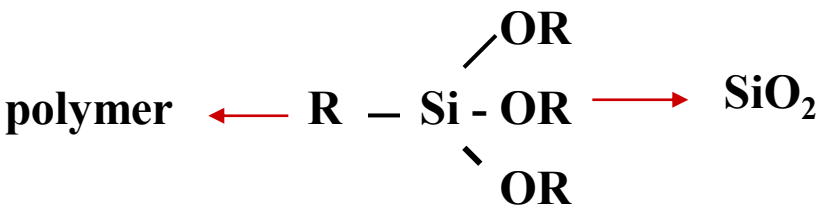
Beijing Zhongke Saina Glass Technology

Scratch resistant coatings on plastics

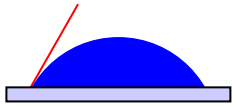


Sol-gel coating

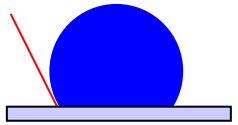




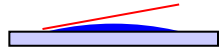
Antifogging and antisoiling glass coatings



glass under atmospheric conditions



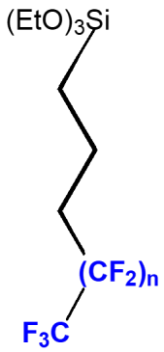
glass modified with a hydrophobic coating



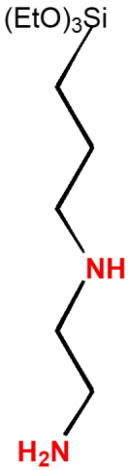
glass modified with a hydrophilic coating

Modification of the glass surface tension

© INM - Saarbrücken - Germany

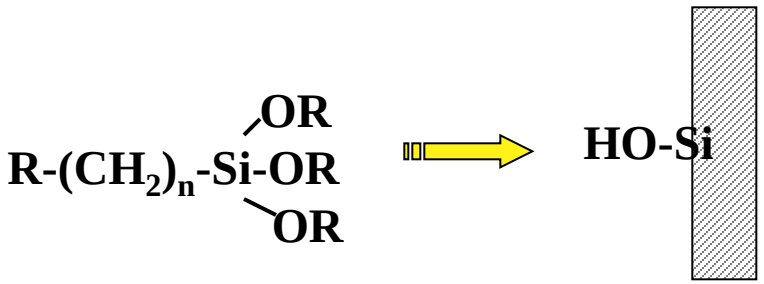


Antisoiling properties



Antifogging properties

hydrophobic coatings on windshields



R = hydrophobic group : CF_3, CH_3, …

Hybride PDMS + TEOS : « sliding effect »

Hybride PDMS + TEOS + FAS : against rain

FAS = CF_3-$(CF_2)_7$-CH_2-CH_2-Si-$(OCH_3)_3$

Central Glass Japon

Sol-gel hydrophobic coatings

G. Schottner, Chem. Mater. 13 (2001) 3422

Stainless steel without coating

Stainless steel with an abrasion resistant fluorinated hybrid coating

Hhydrophilic and photocatalytic coatings

Two layers :

SiO_2 : hydrophilic, scratching resistant

TiO_2 : photocatalytic effect under UV irradiation

Thermal treatment at 600°C

Seiji: Yamazaki
Glass Research Center, Central Glass Co. Ltd., 1510 Ohkuchi-cho, Matsusaka-shi, Mie,
E-mail seiji.yamazaki@cgco.co.jp

‘anti-mist’ coatings

Central Glass - Japon

To avoid moisture condensation on a cold surface

SiO_2-ZrO_2

Nobuyuki.Itakura,
Glass Research Center, Central Glass Co. Ltd.,
1510 Ohkuchi-cho, Matsusaka-shi, Mie, 515-0001 Japan
E-mail nobuyuki.itakura@cgco.co.jp

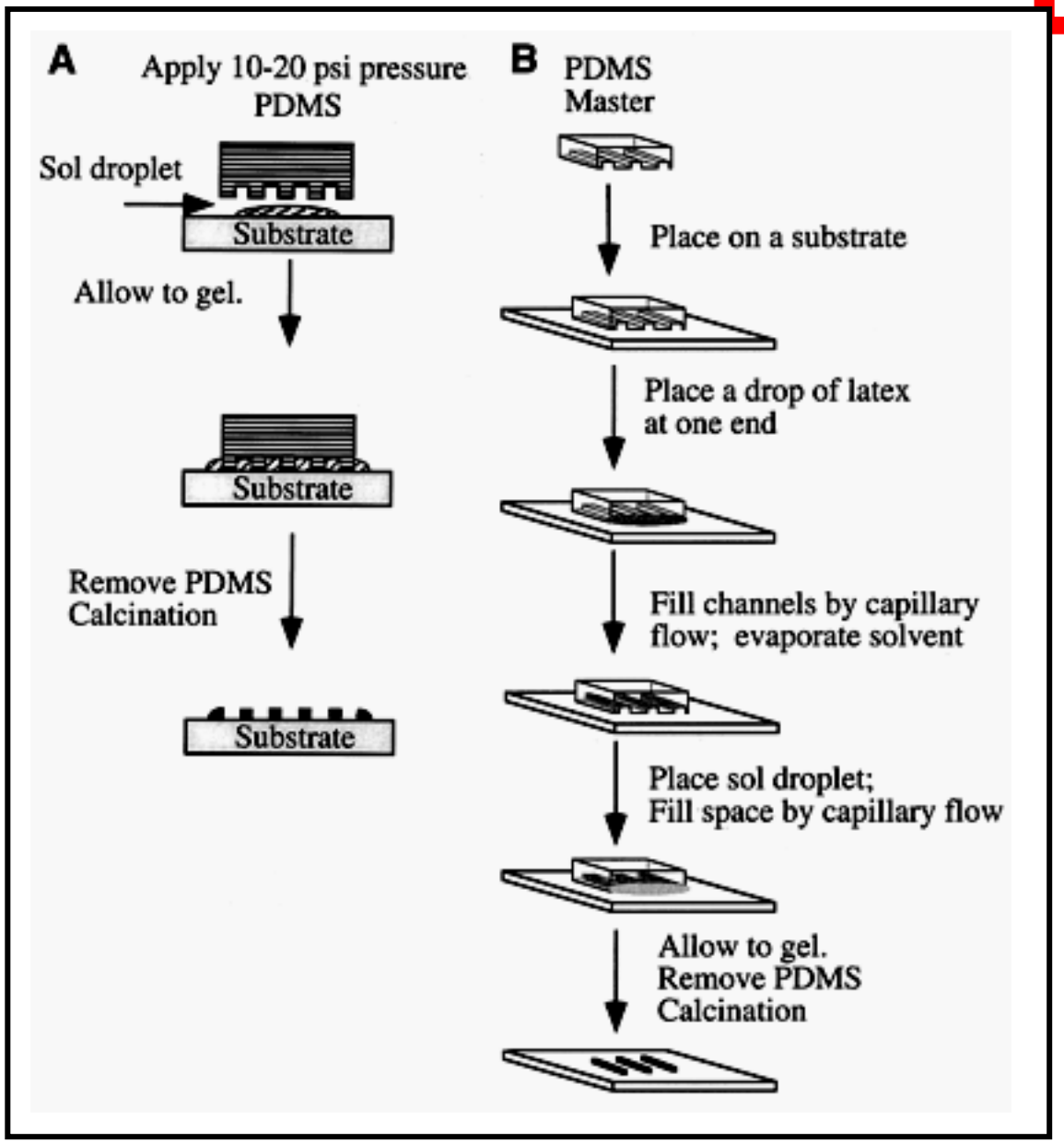
SiO_2 / ZrO_2 colloïdal + top-layer SiO_2 ou

Gel = isocyanate + ethylene oxide/propylene oxide + PEG + PC polyol

dépôt par spin-coating + traitement thermique (@150°C); ép. 20µm

Nanopatterning via sol-gel embossing

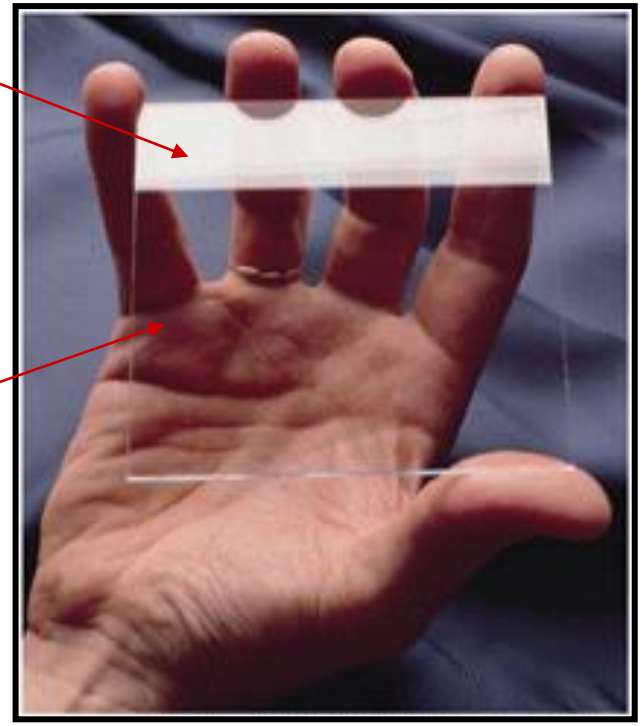
soft hybrid sol-gel films



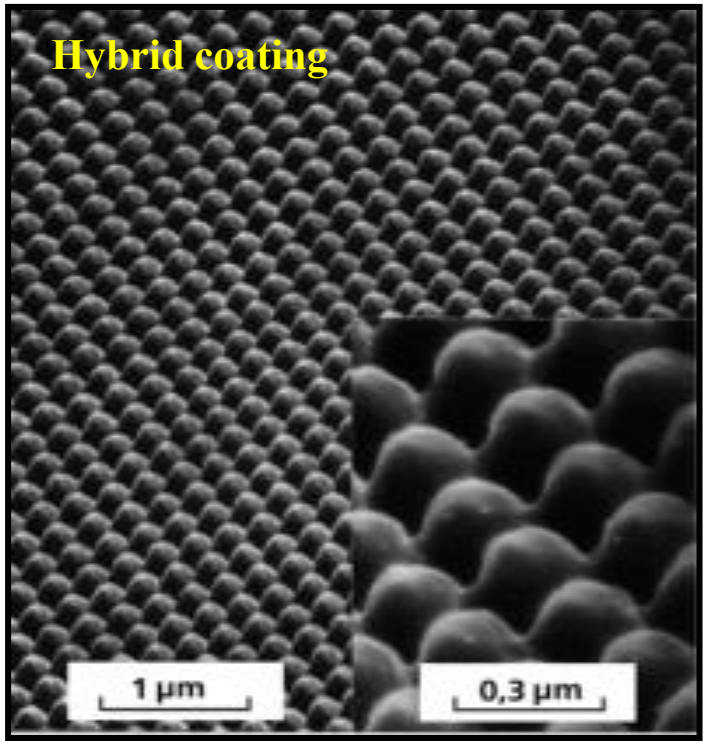
Nano-patterned films

produced by embossing a hybrid coating

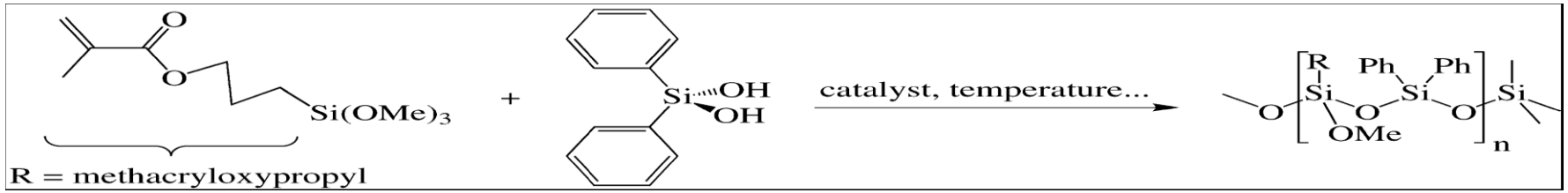
Periodic microstructure leading to a gradient in the refractive index

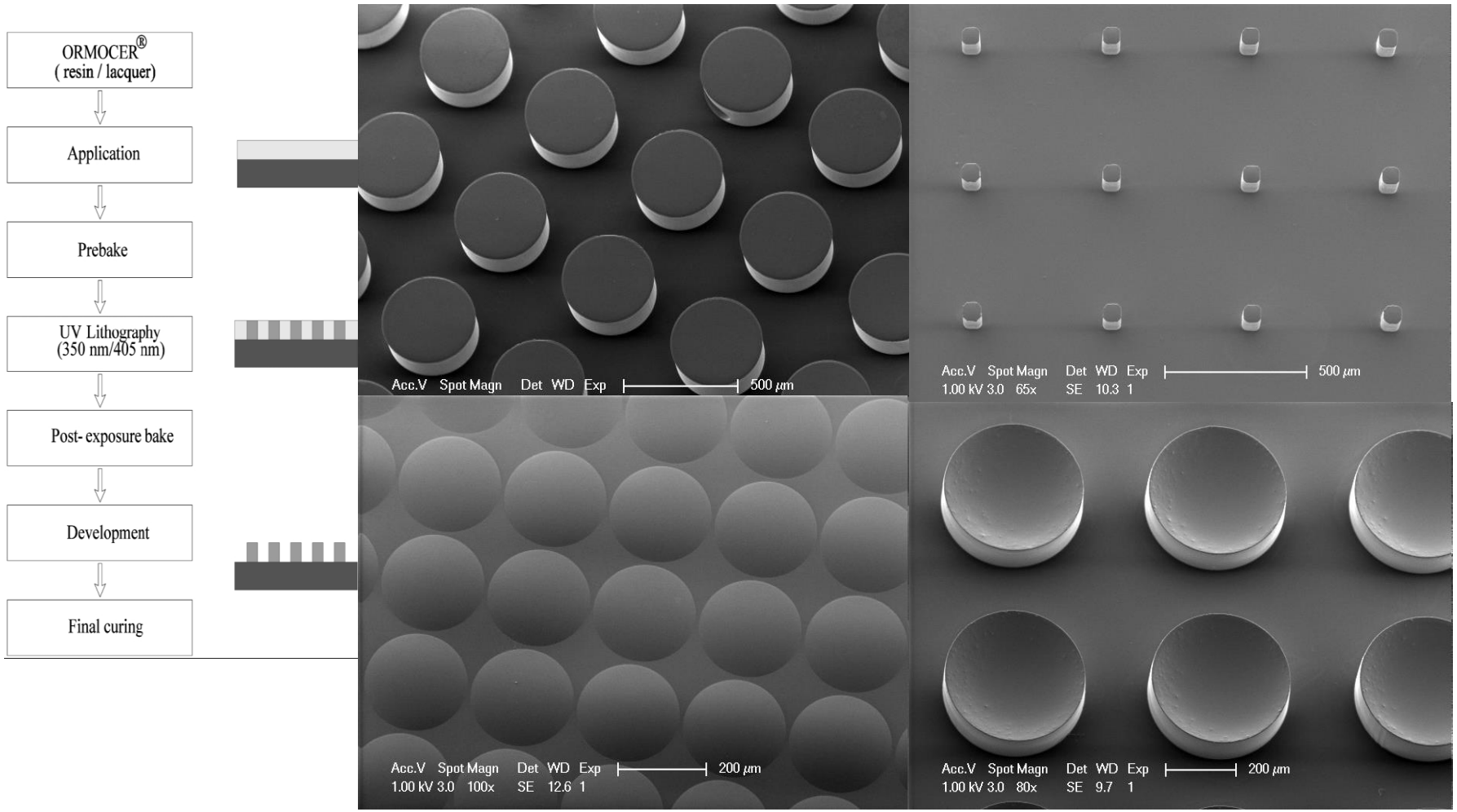


' lotus ' effect



Photosensitive Sol-Gel





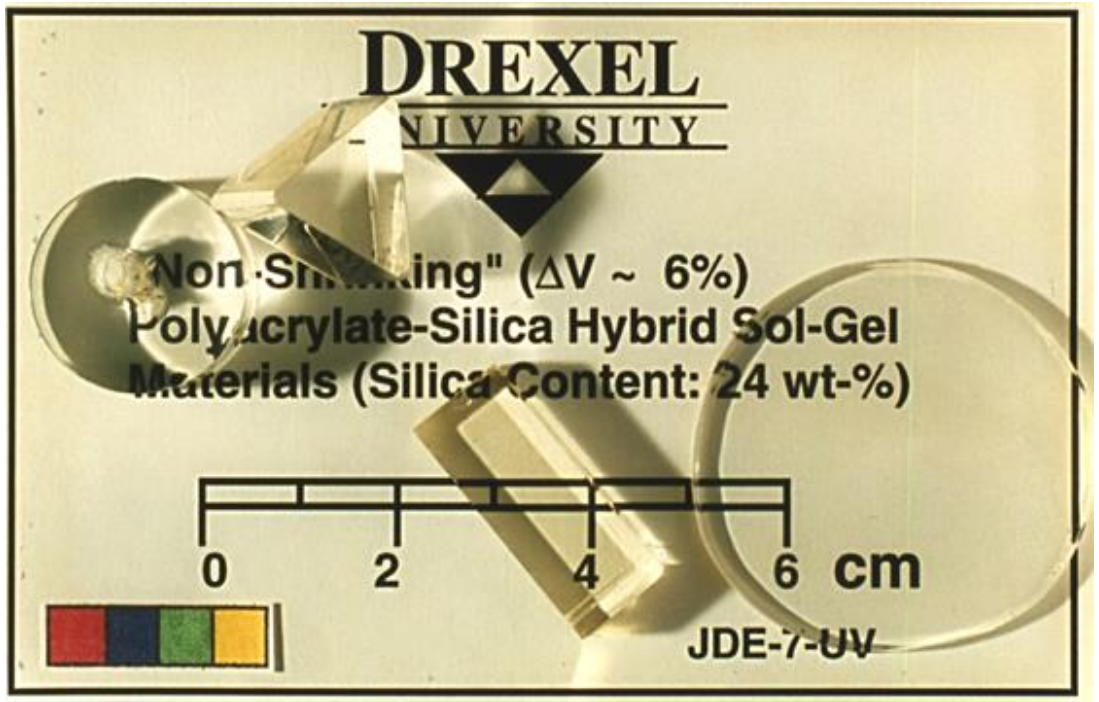
sol-gel optics

bulk pieces

no crack or shrinkage upon drying (hydrophobic organics)

easily shaped materials (molding, polishing)

nano-composite = transparency

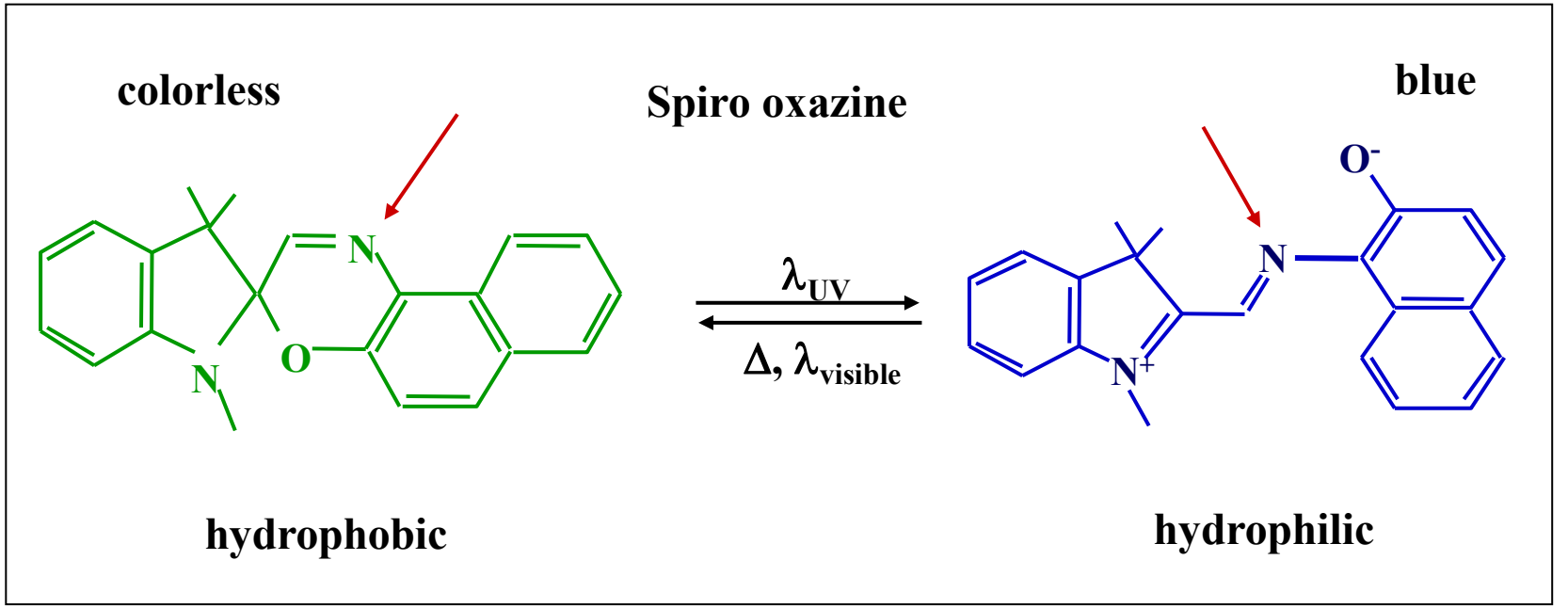


sol-gel optics

Organic dyes in a silica matrix

fluorescence - laser - NLO - photochromism

Photochromic glasses



Hydrophilic silica ⟹ **switching time ≈ 1 hour**