微纳光电子材料与器件工艺原理

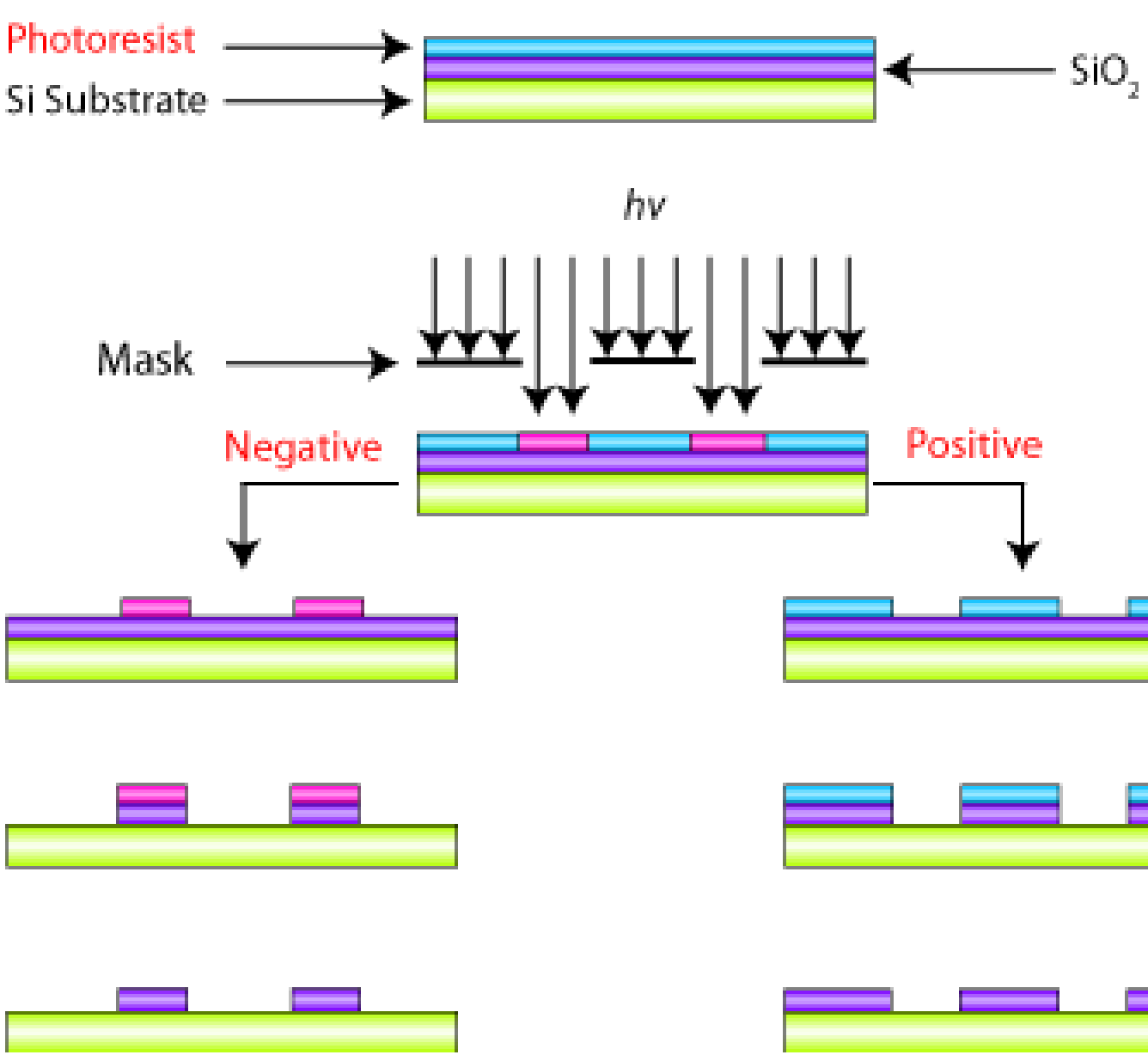
Photolithography 光刻
Part II: Photoresists

Xing Sheng 盛 兴

Department of Electronic Engineering
Tsinghua University
xingsheng@tsinghua.edu.cn

Photolithography

光刻胶



负胶

正胶

Photolithography

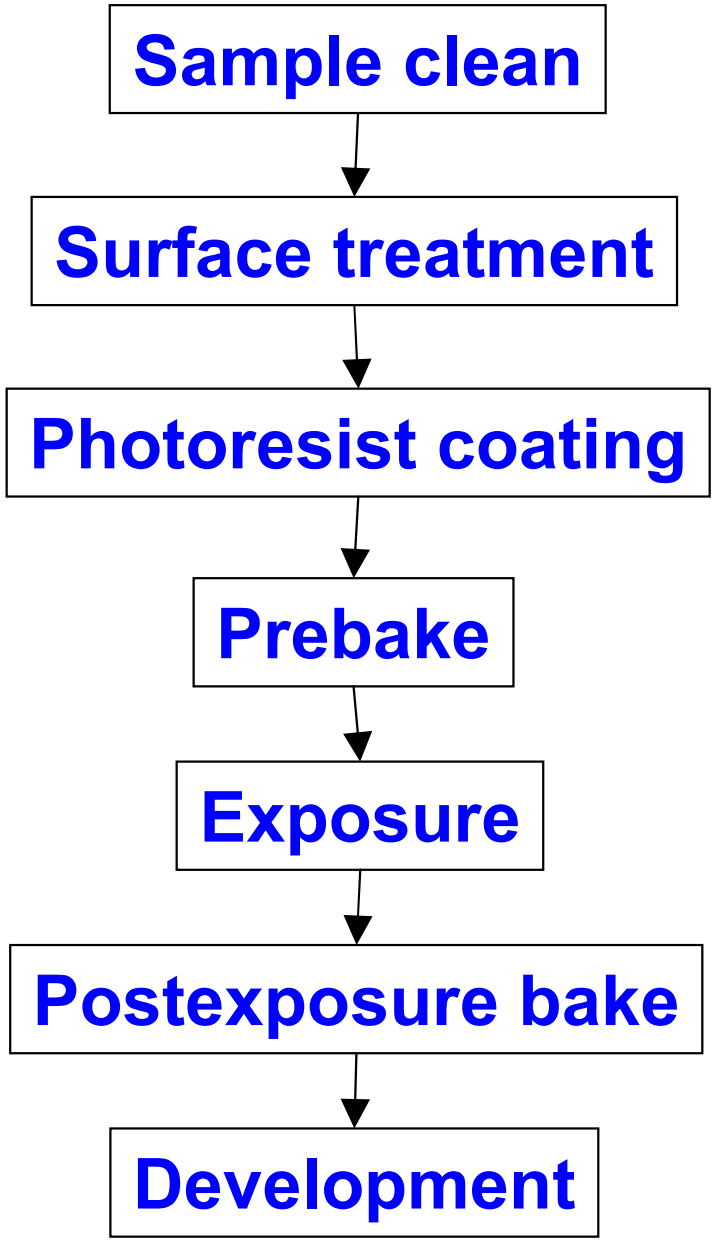
Dark room

photography

Yellow zone

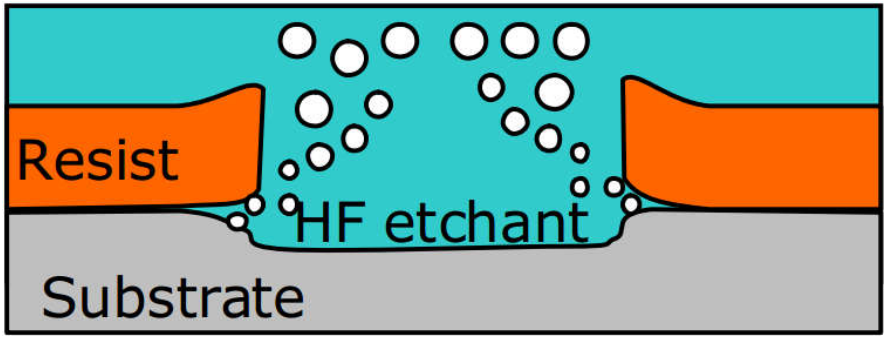
avoid UV exposure!

Photolithography



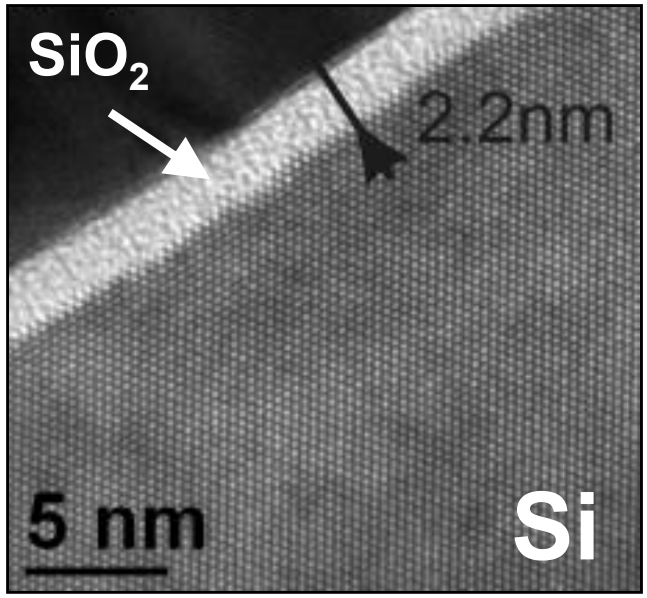
Photoresist Adhesion: Issues

- Hydrophobic (疏水)
  - clean Si, some polymers, ...
- Hydrophilic (亲水)
  - SiO_2, metals (Ag, Au), some polymers, ...
- Most photoresists are hydrophobic (疏水)
  - adhesion problems on glass, Ag, Au, ...

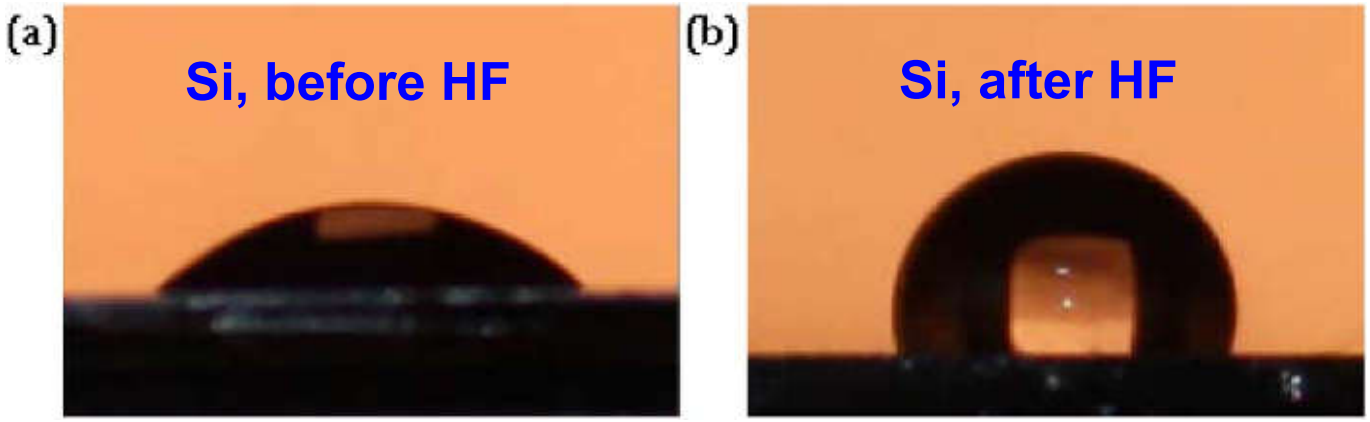


Photoresist Adhesion: Solutions

- **Surface clean**
  - wet clean
  - for Si, use HF to remove SiO_2
  - plasma treatment



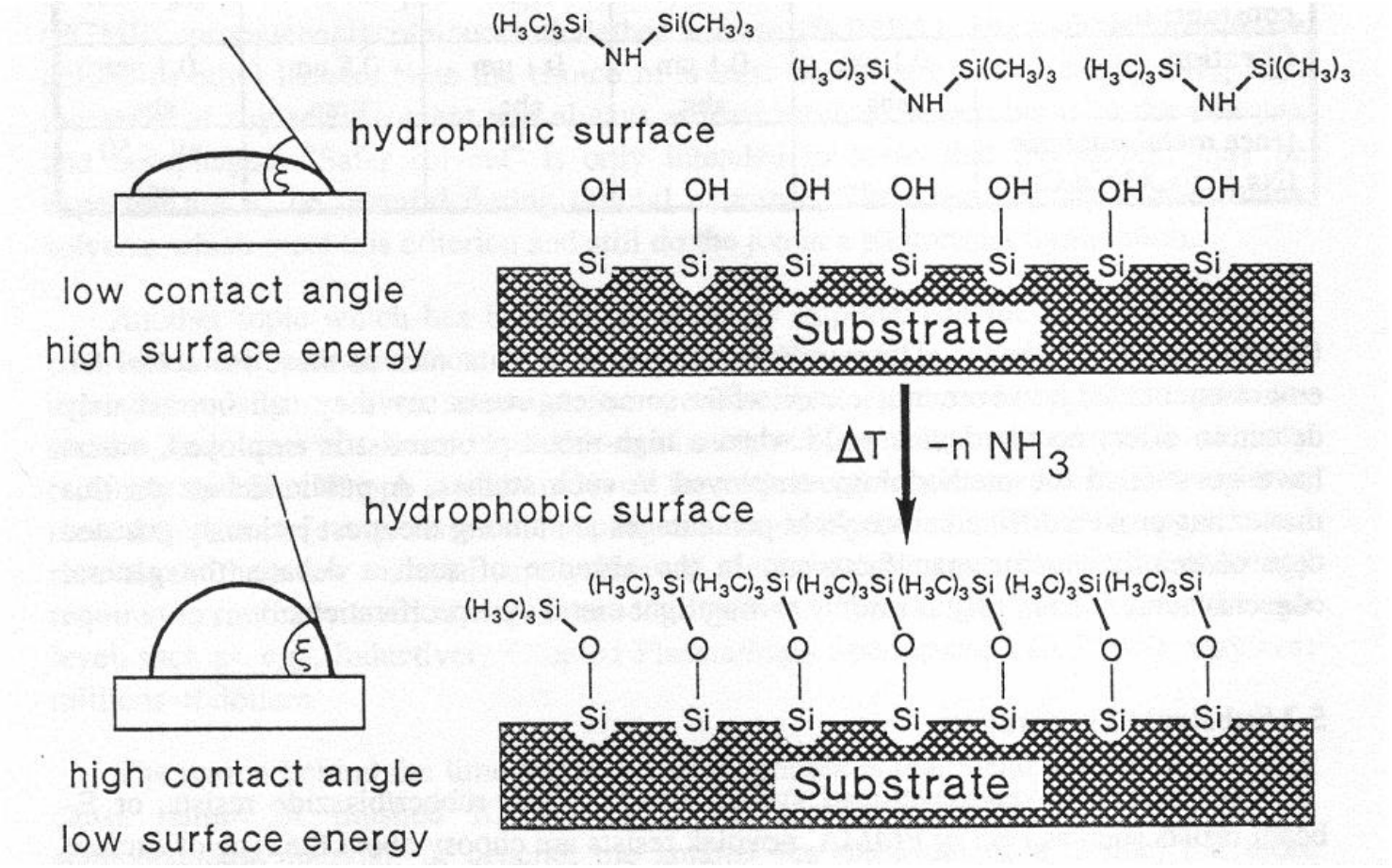
- **Dehydration bake**
  - remove water from sample surface



Q: Why?

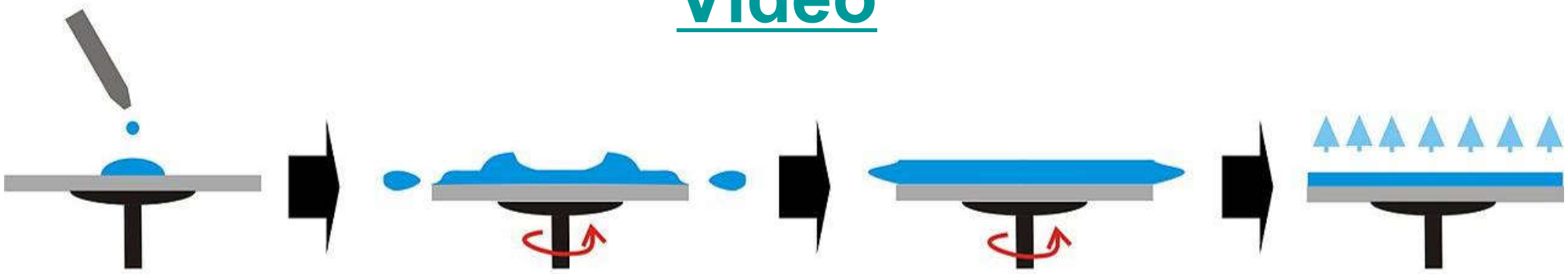
Photoresist Adhesion: Solutions

- **Adhesion promoter**
  - **self-assembled monolayer (SAM)**



Spin Coating

Video



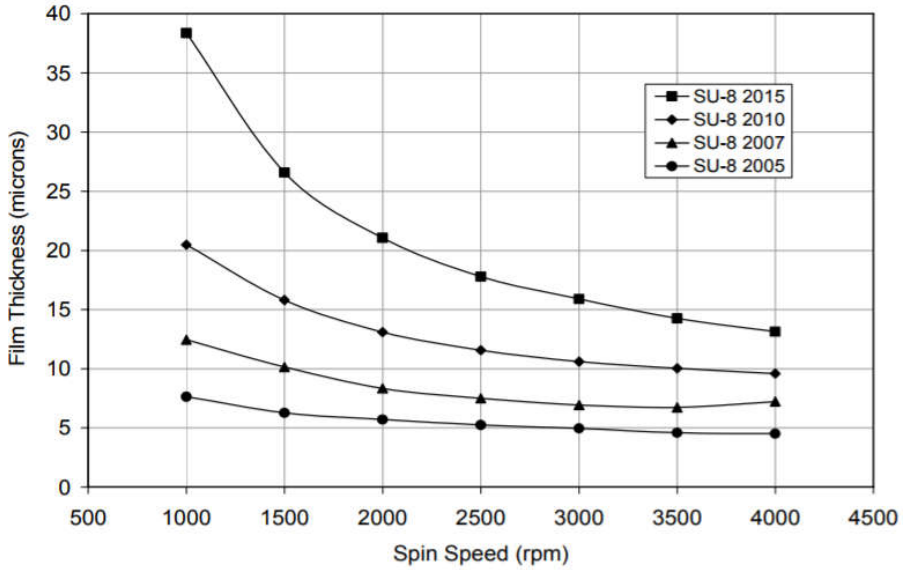
thickness $h \sim \left(\frac{\mu}{t\omega^2}\right)^{1/2}$

h	thickness
μ	viscosity
t	time
ω	speed

https://www.ossila.com/pages/spin-coating

Spin Coating – Film Thickness

thickness vs. speed and viscosity

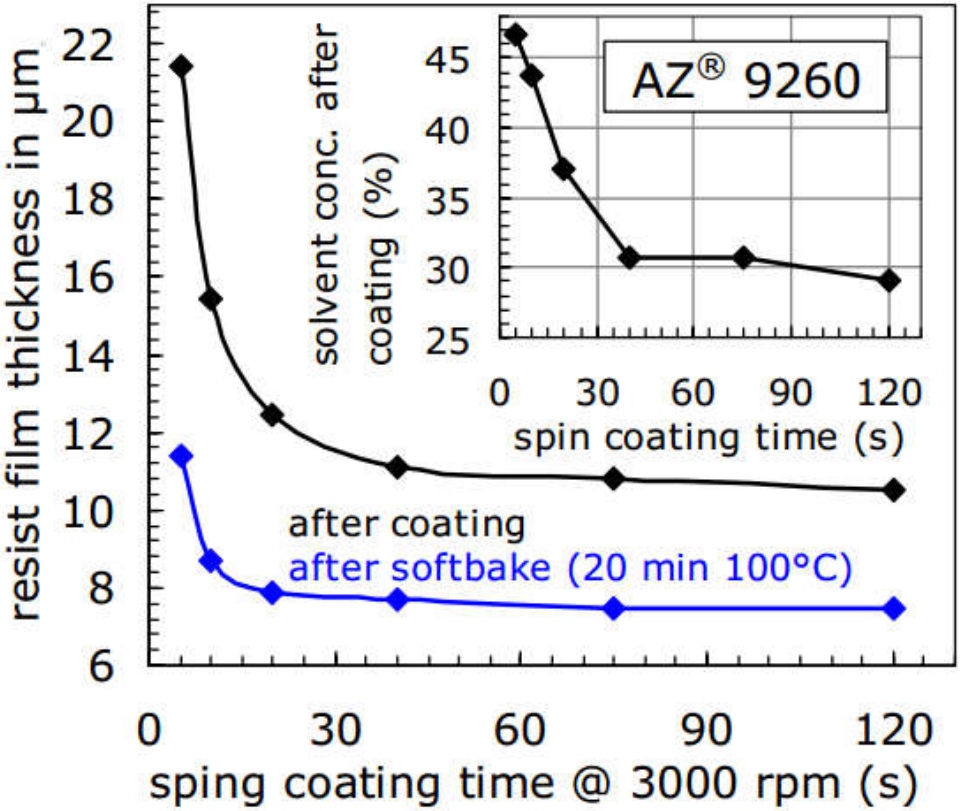


$$h \sim \left(\frac{\mu}{t\omega^2}\right)^{1/2}$$

SU-8 2000	% Solids	Viscosity (cSt)	Density (g/ml)
2000.5	14.3	2.49	1.070
2002	29.00	7.5	1.123
2005	45.00	45	1.164
2007	52.50	140	1.175
2010	58.00	380	1.187
2015	63.45	1250	1.200

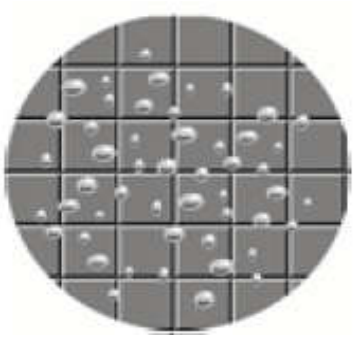
Spin Coating – Film Thickness

thickness vs. spin time

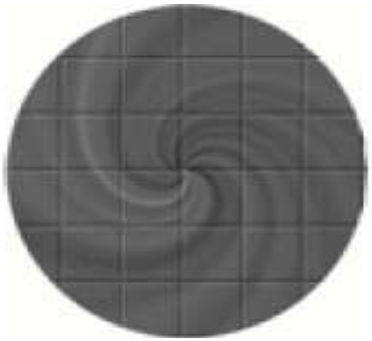


$$h \sim \left(\frac{\mu}{t\omega^2}\right)^{1/2}$$

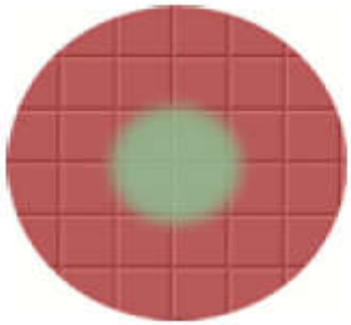
Spin Coating - Troubleshooting



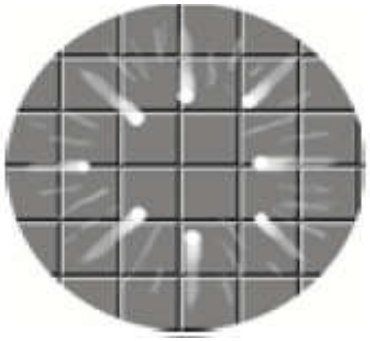
- bubbles in resist
- sample not clean
- N_2 generation



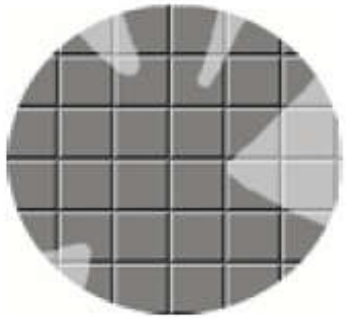
- accelerate too fast
- sample off center
- time too short
- evaporate too fast



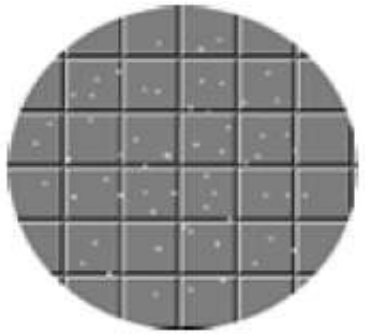
- improper chuck
- sample off center



- accelerate too fast
- sample off center
- sample not clean



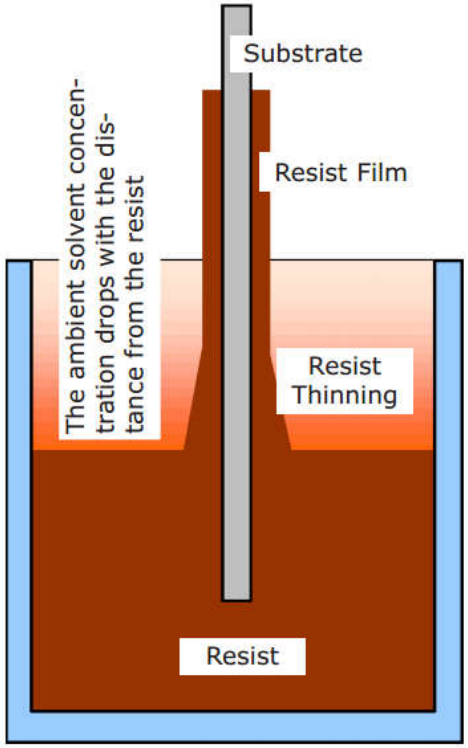
- fluid too little
- sample dewet
- sample not clean



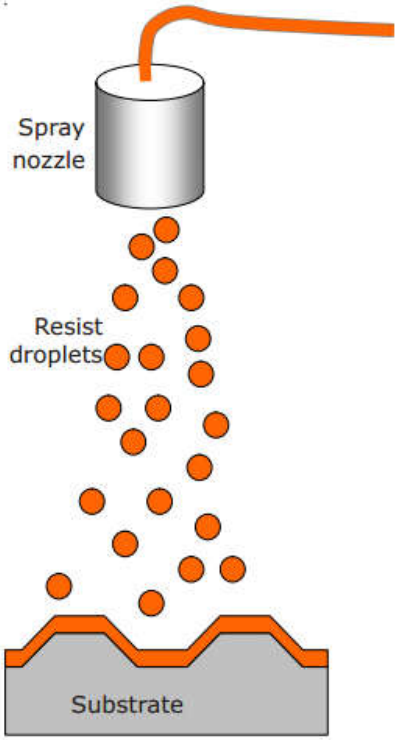
- sample not clean
- resist not clean

Other Coating Methods

- **When spin coating is difficult ...**
  - **too thick, sample is not uniform, ...**
  - **save resists**



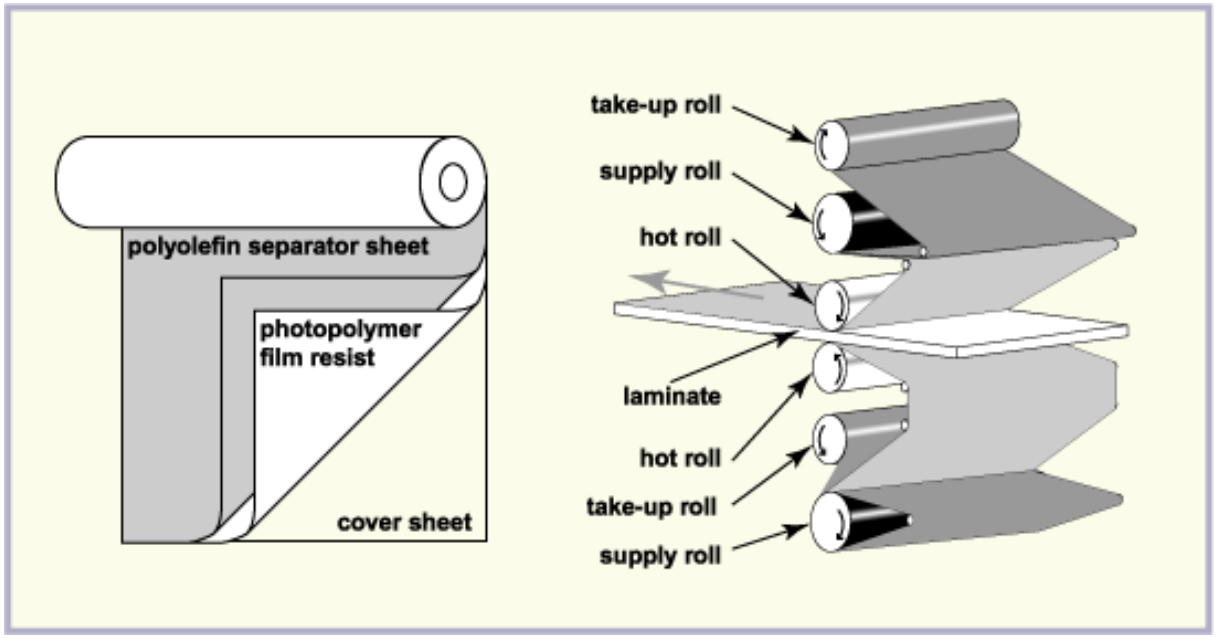
dip coating

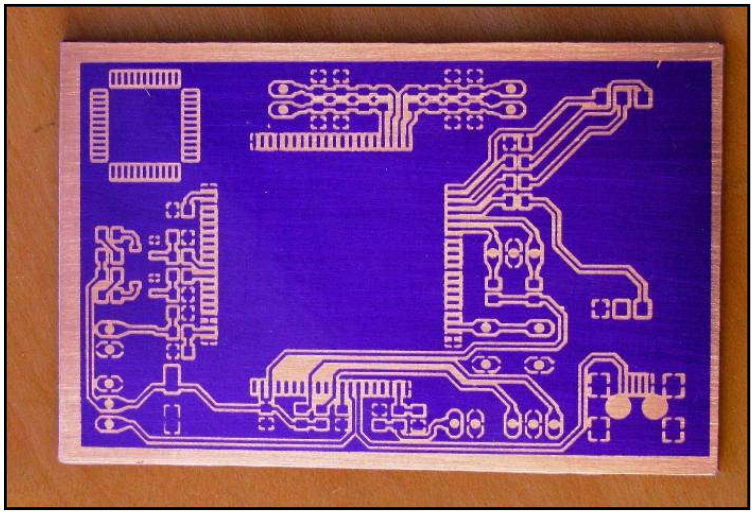


spray coating

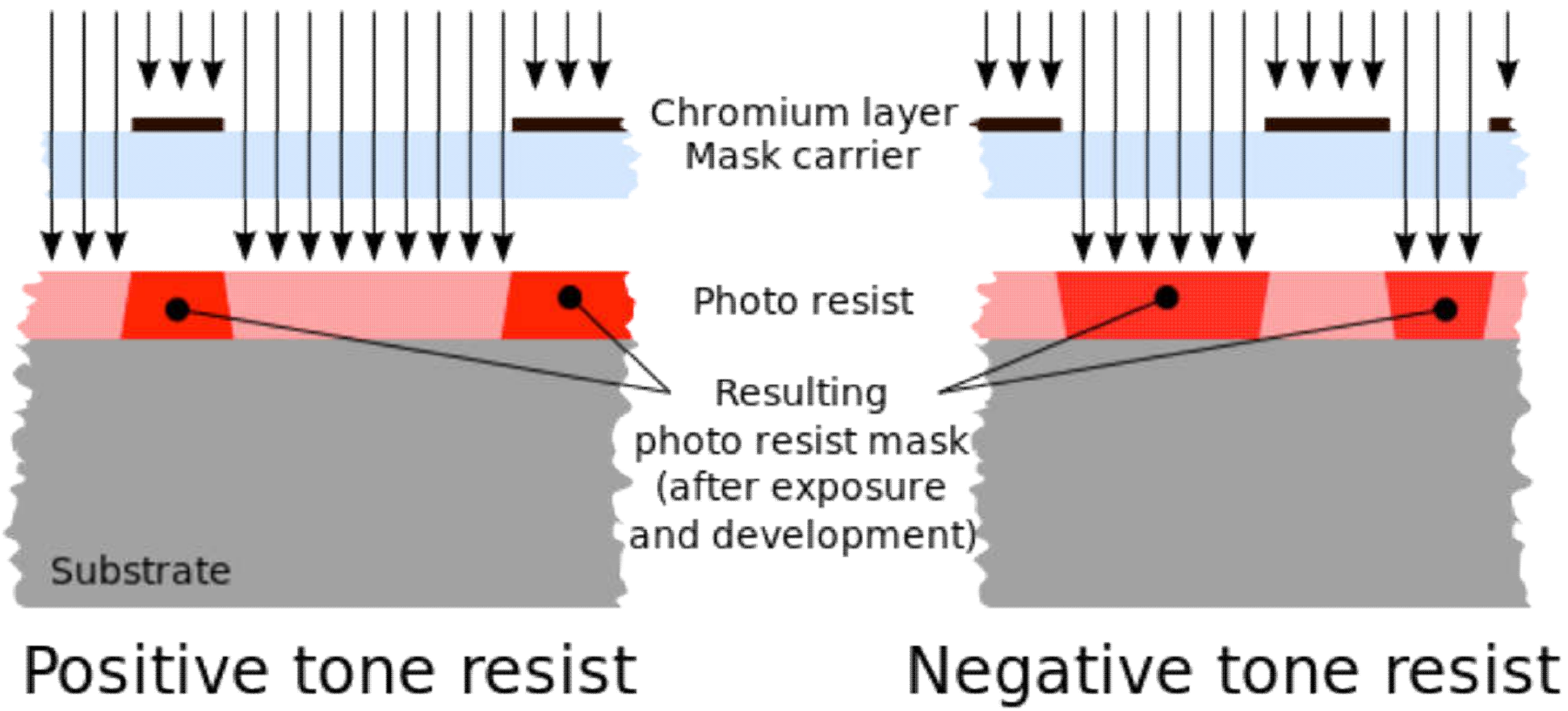
Dry Resist

- **Thick film, for PCB making**





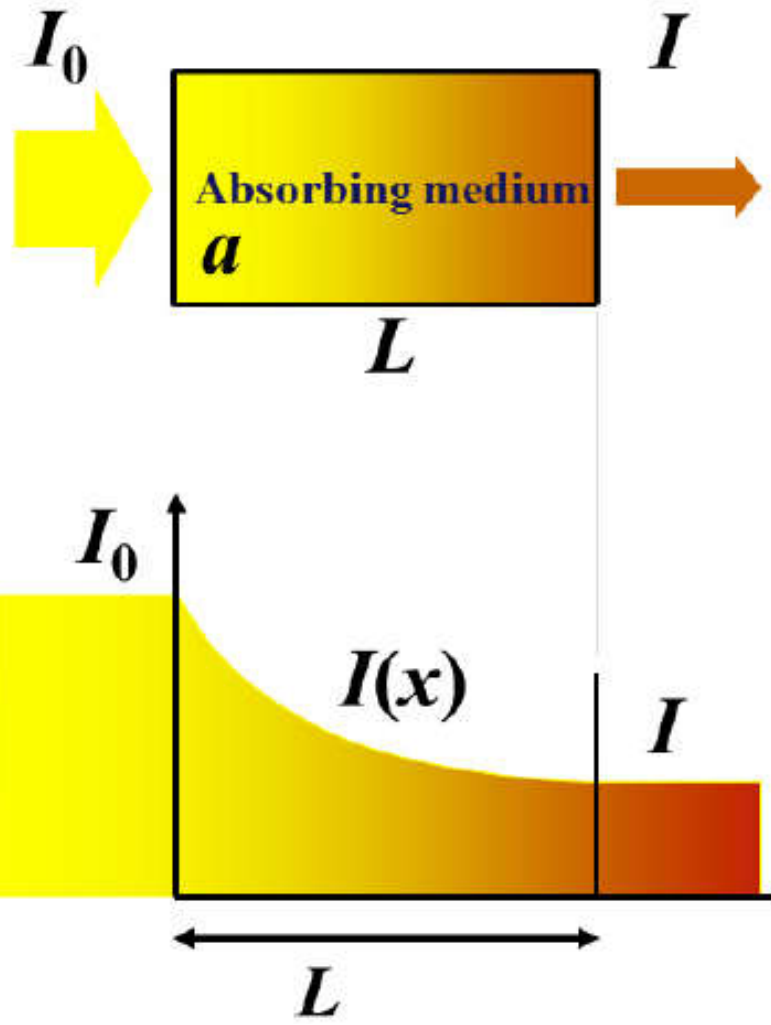
Exposure


Chromium layer
Mask carrier
Photo resist
Resulting
photo resist mask
(after exposure
and development)
Substrate
Positive tone resist
Negative tone resist

Optical Absorption

Lambert Beer's law

$$I = I_0 \exp(-\alpha L)$$



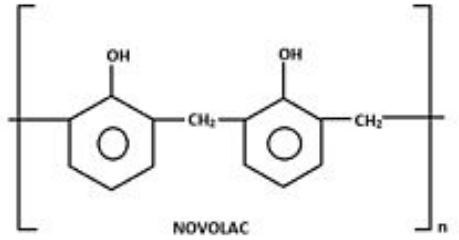
thicker films require larger exposure dose

THICKNESS microns	EXPOSURE ENERGY mJ/cm^2
0.5 - 2	60 - 80
3 - 5	90 - 105
6 - 15	110 - 140
16 - 25	140 - 150
26 - 40	150 - 160

example: SU-8 resist

Positive Resist: Example

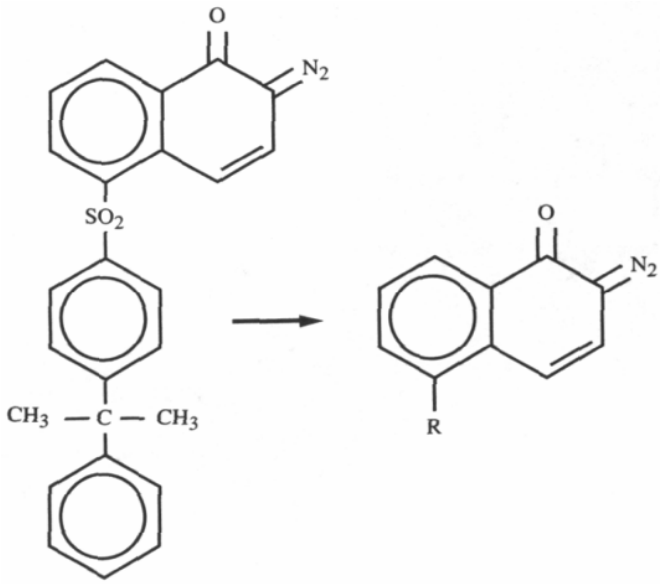
- **Base resin**
  - novolac



novolac

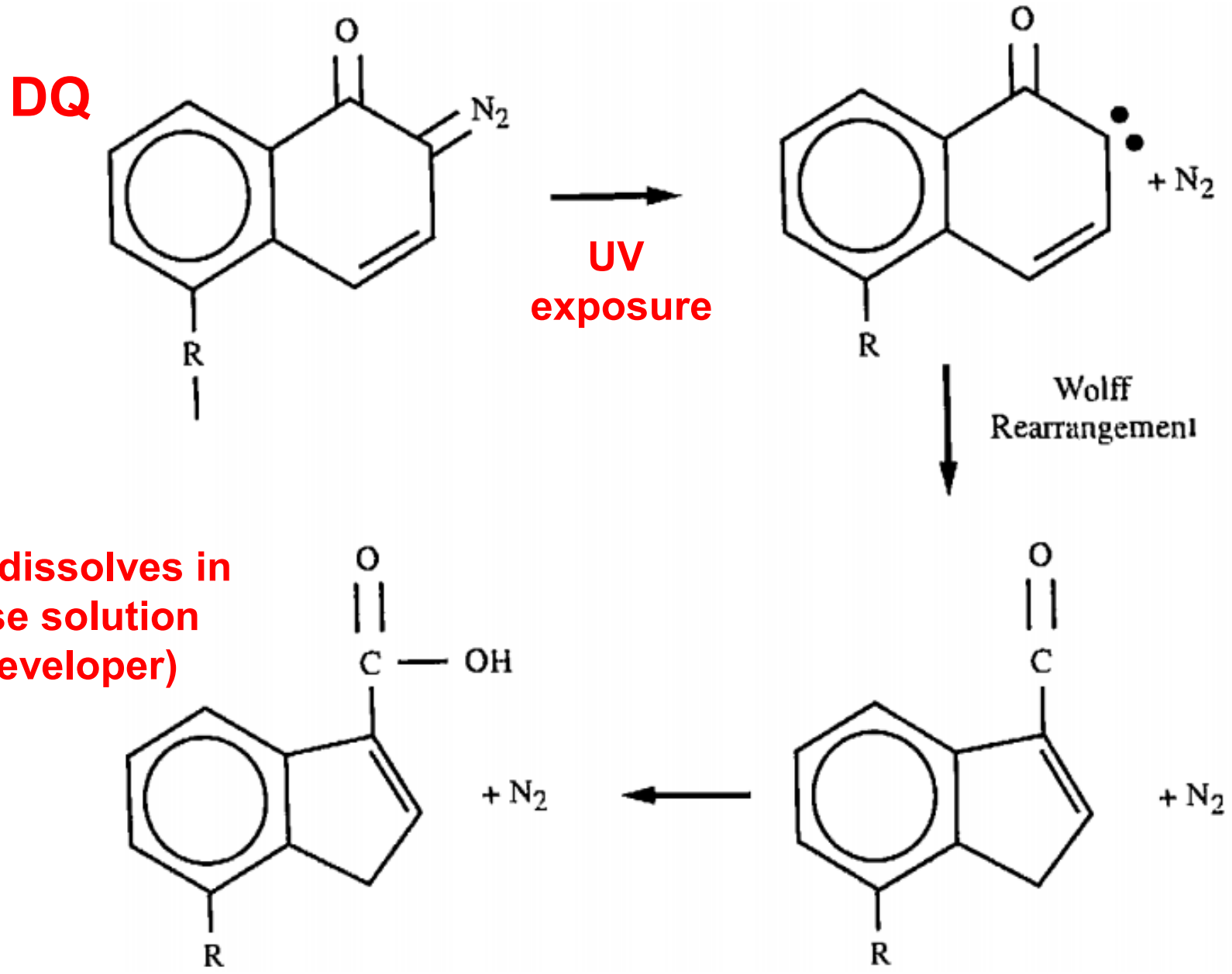
- **Photoactive compound (PAC)**
  - diazoquinone (DQ)
  - photosensitive

- **Solvent**
  - n-butyl acetate, xylene, ...
  - volatile
  - control viscosity, film thickness, ...



DQ

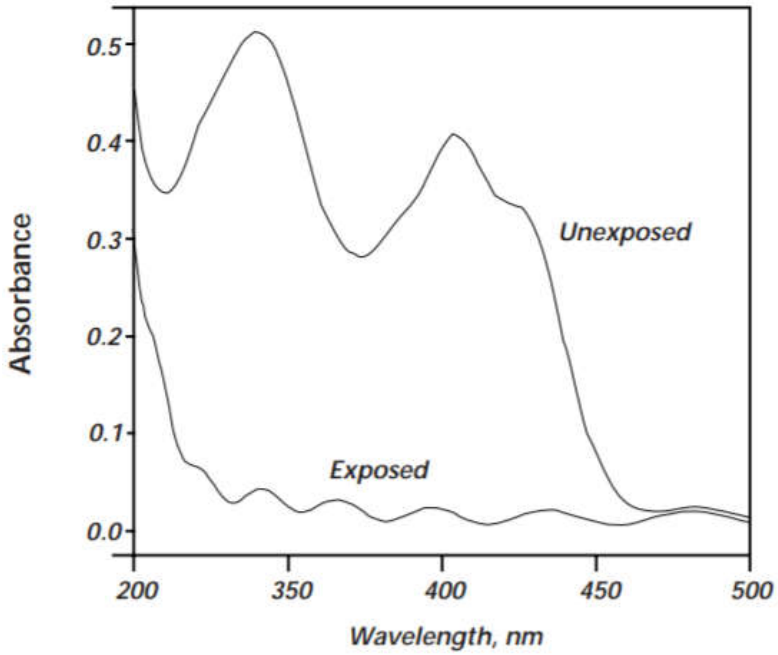
Positive Resist: Example

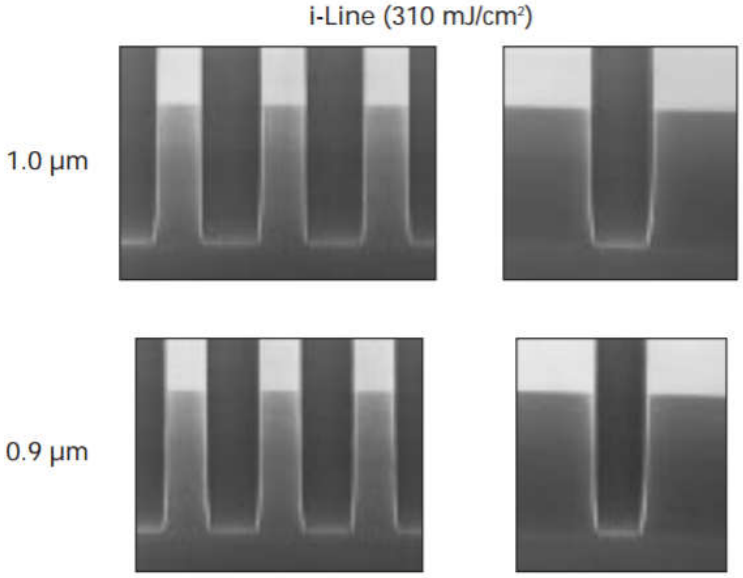


Positive Resist: Example

Process for SPR220-v3.0

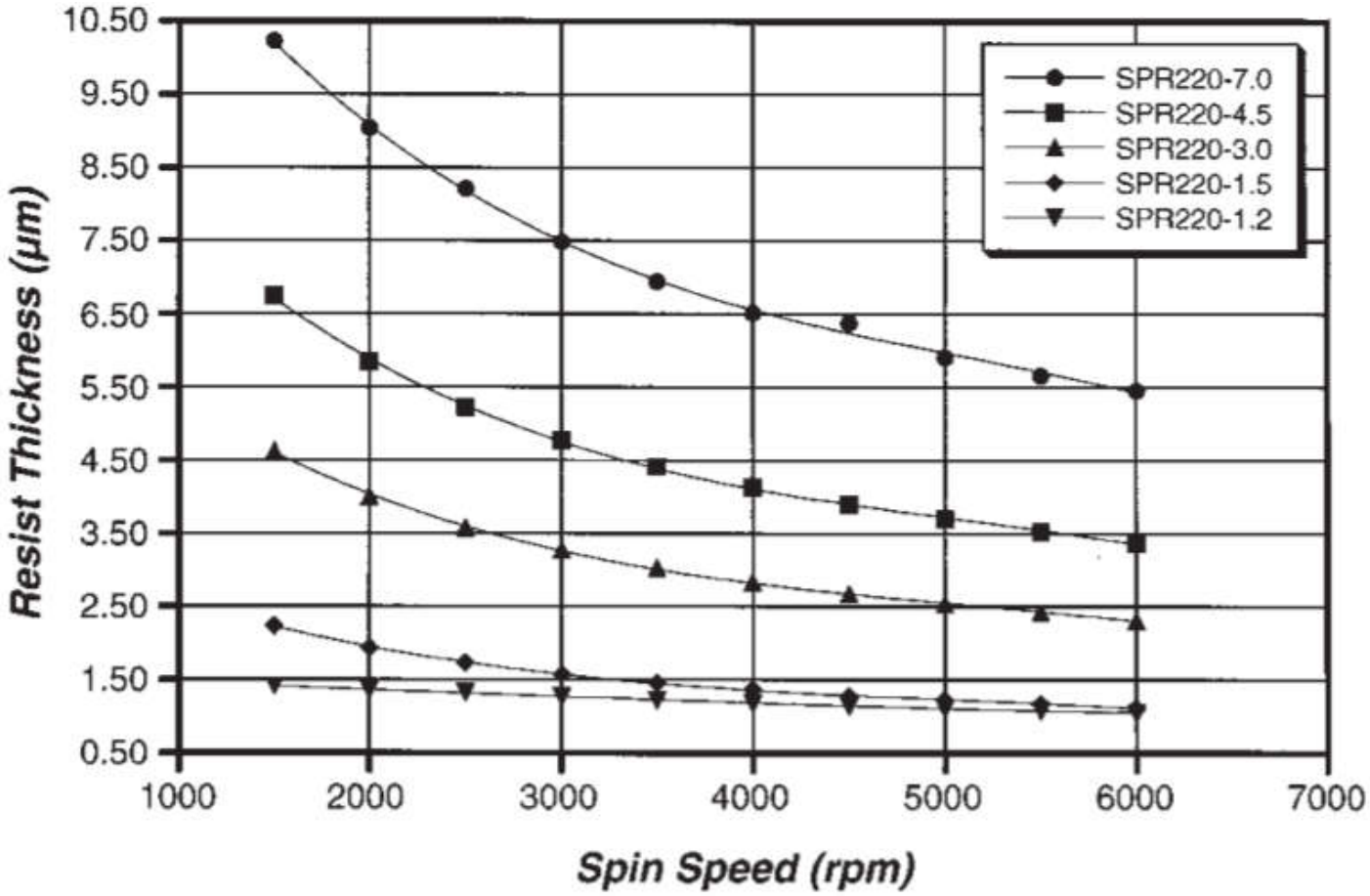
- clean sample (glass or silicon)
  - acetone / isopropanol / DI water, N_2 gas blow
- dehydration bake at 110 C, 10 mins
  - remove moisture
- spin coat SPR220-v3.0, 3000 rpm, 40 sec
- soft bake at 110 C, 90 sec
  - evaporate solvent
- UV expose (i-line), 300 mJ/cm^2
- post-exposure bake at 110 C, 90 sec
  - stabilize the resist (optional)
- develop in MIF300 (alkali developer), 1 min
- hard bake
  - make resist robust during etching





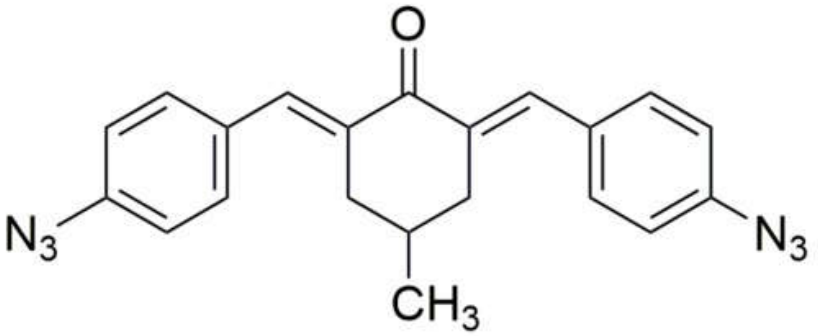
Positive Resist: Example

- **film thickness**
  - **depend on solvent concentration, spin speed, etc**

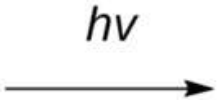


Negative Resist: Example

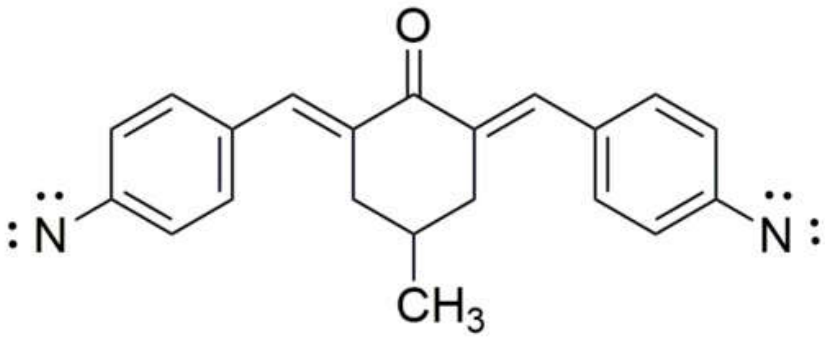
soluble in organic developer



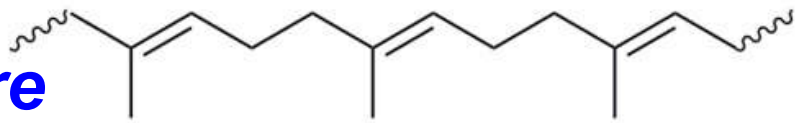
2 ,6- bis(4-azidobenzal)-4-4methlcyclohexanone



UV exposure



Negative resists are long-chain polymers



polyisoprene

heating

Crosslinked insoluable polymer

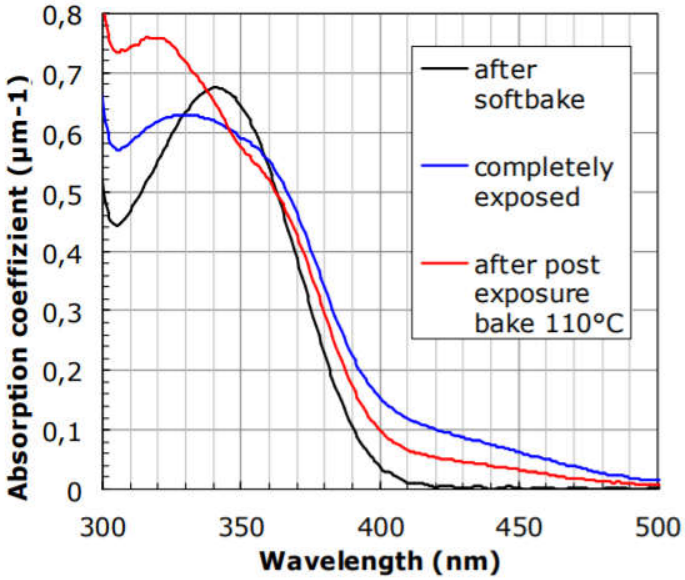
only used for features > 2 μm

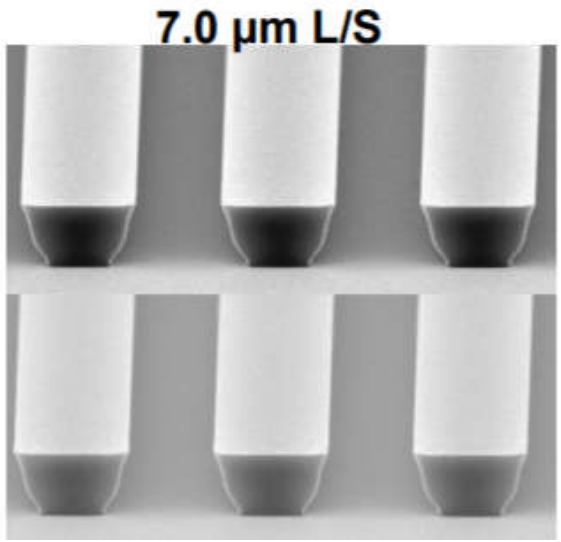
insoluble in organic developer

Negative Resist: Example

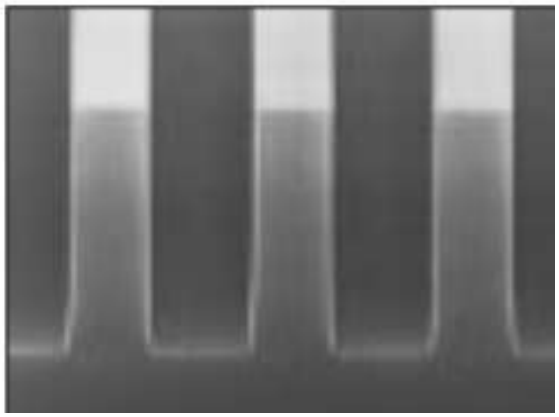
Process for AZ nLoF 2070

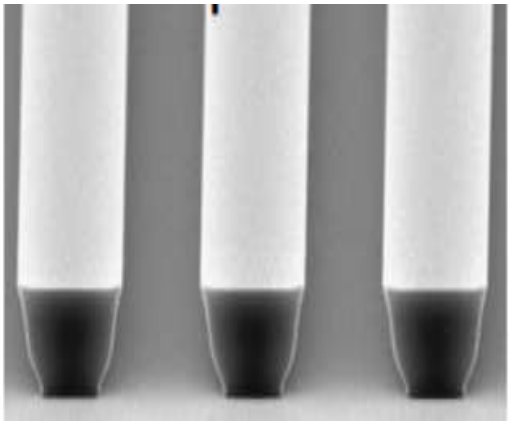
- clean sample (glass or silicon)
  - acetone / isopropanol / DI water, N_2 gas blow
- dehydration bake at 110 C, 10 mins
  - remove moisture
- spin coat AZ nLoF 2070, 3000 rpm, 40 sec
- soft bake at 110 C, 90 sec
  - evaporate solvent
- UV expose (i-line), 50 mJ/cm^2
- post-exposure bake at 110 C, 90 sec
  - cross link resist (*required*)
- develop in MIF300 (alkali developer), 1 min

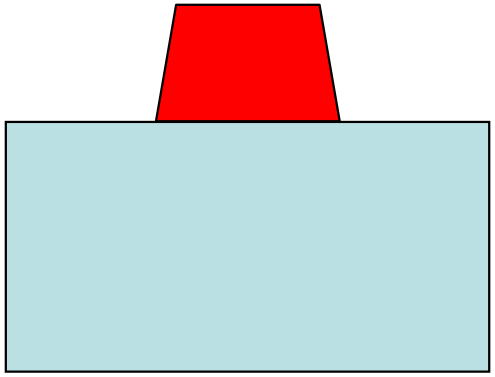


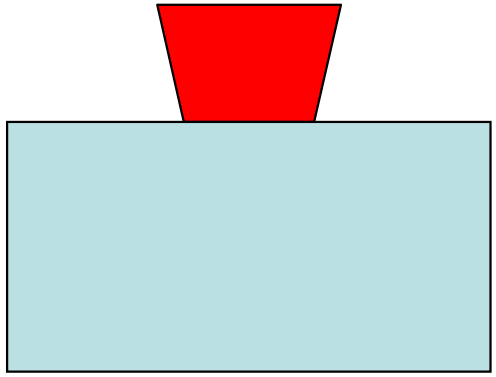


Positive vs. Negative



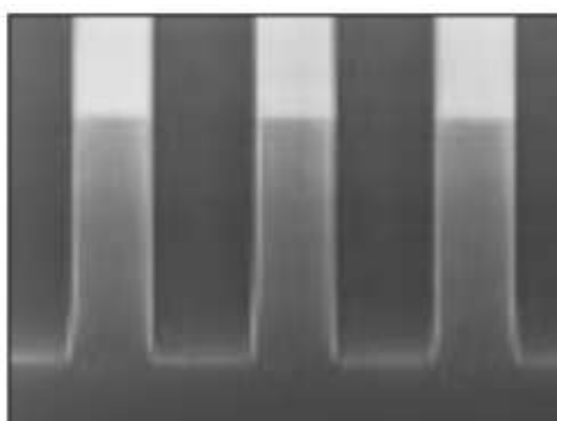


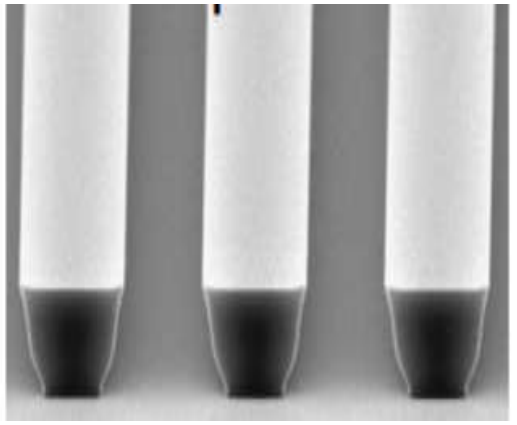


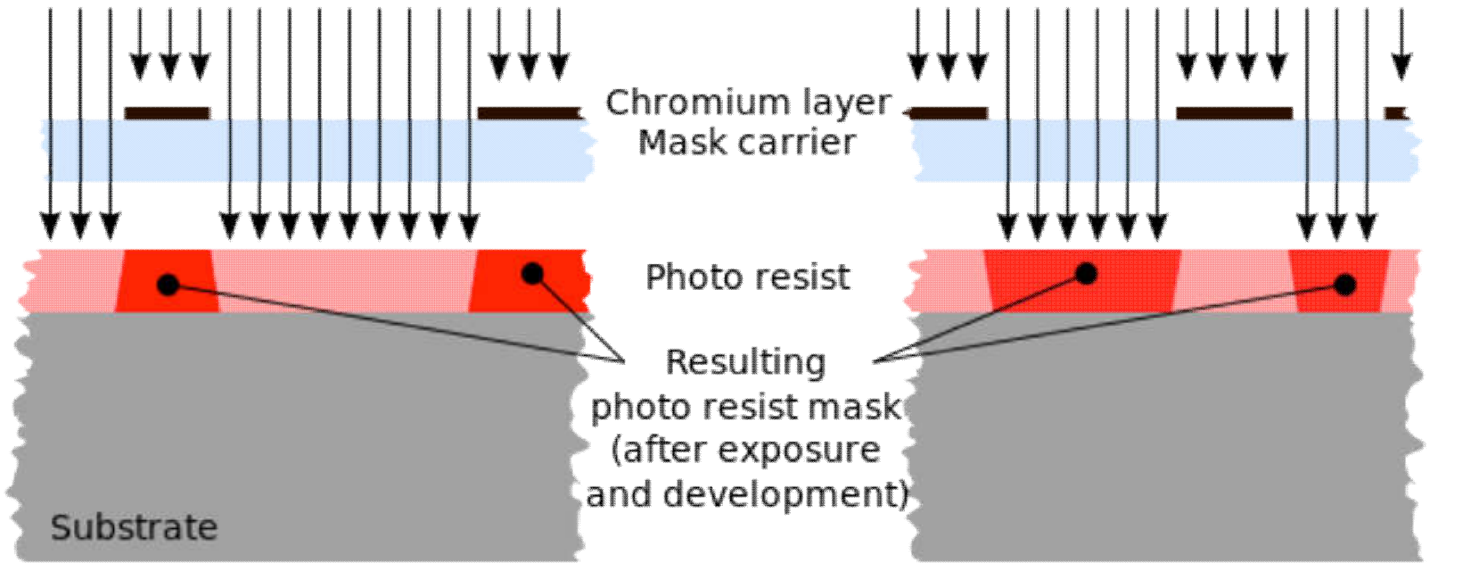


?

Positive vs. Negative





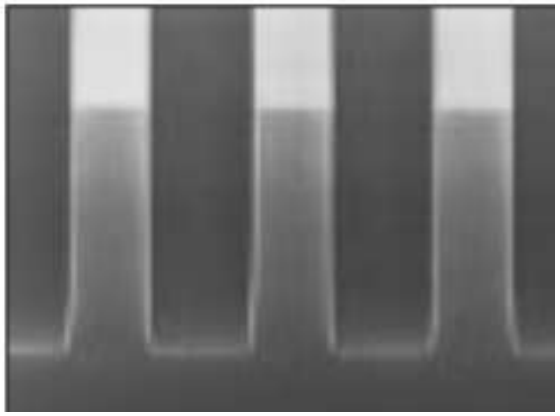


Positive tone resist

Negative tone resist

Lithography - Troubleshooting

positive resist

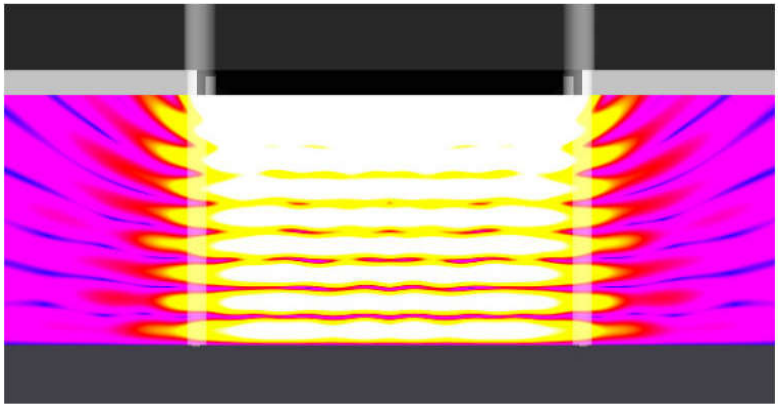


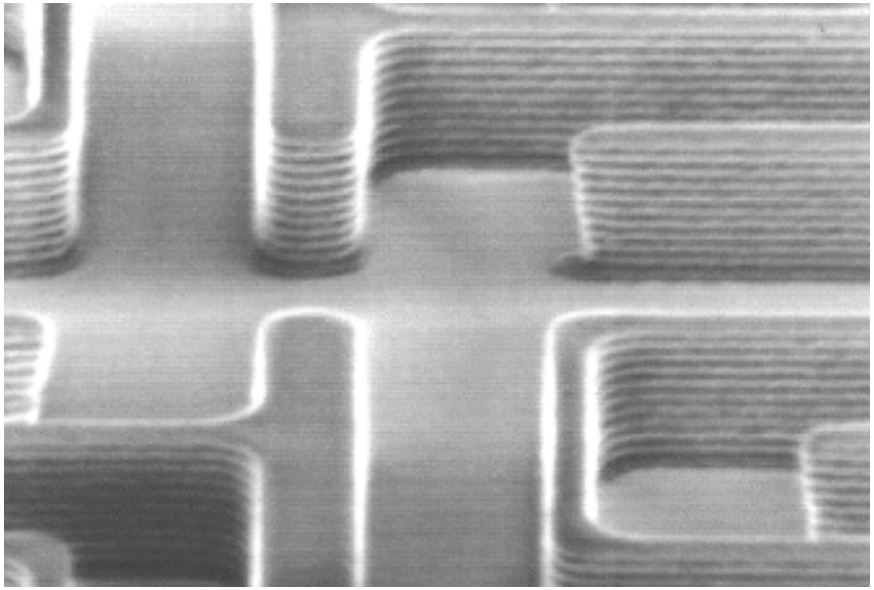
Q: what will happen, if:

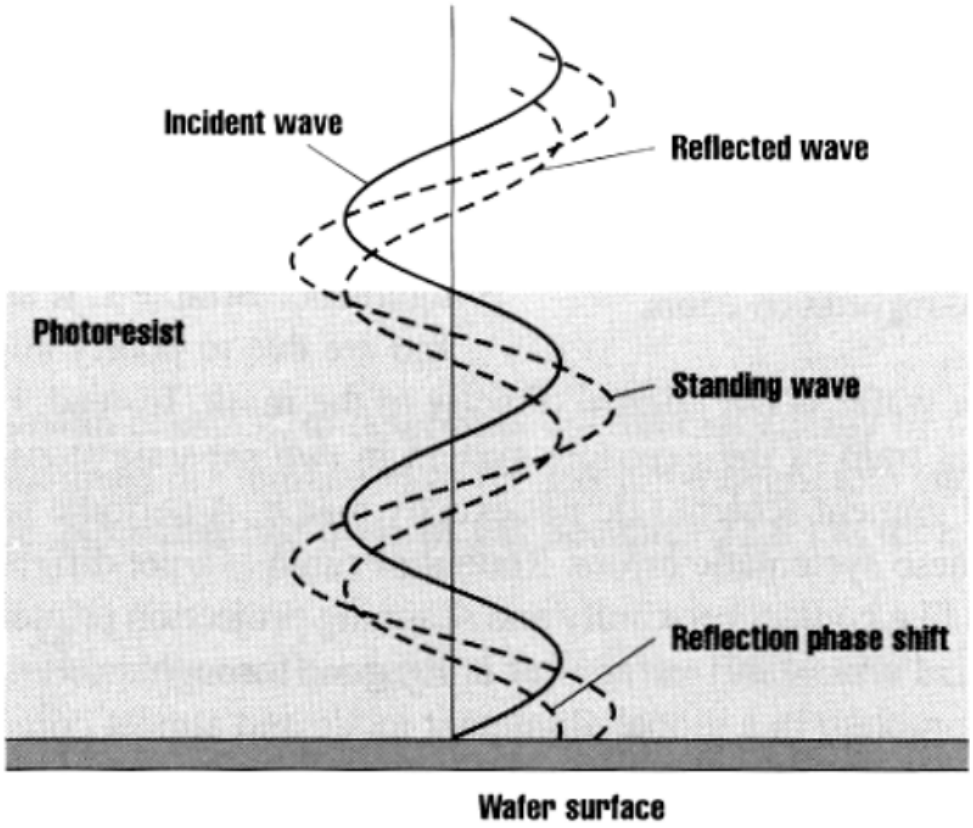
1. under-exposed
2. over-exposed
3. under-developed
4. over-developed

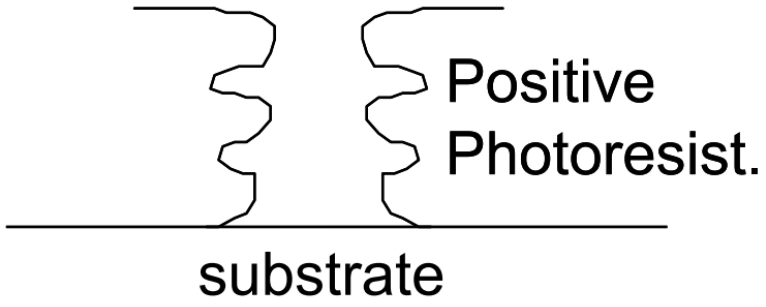
how about negative resist?

Standing Waves

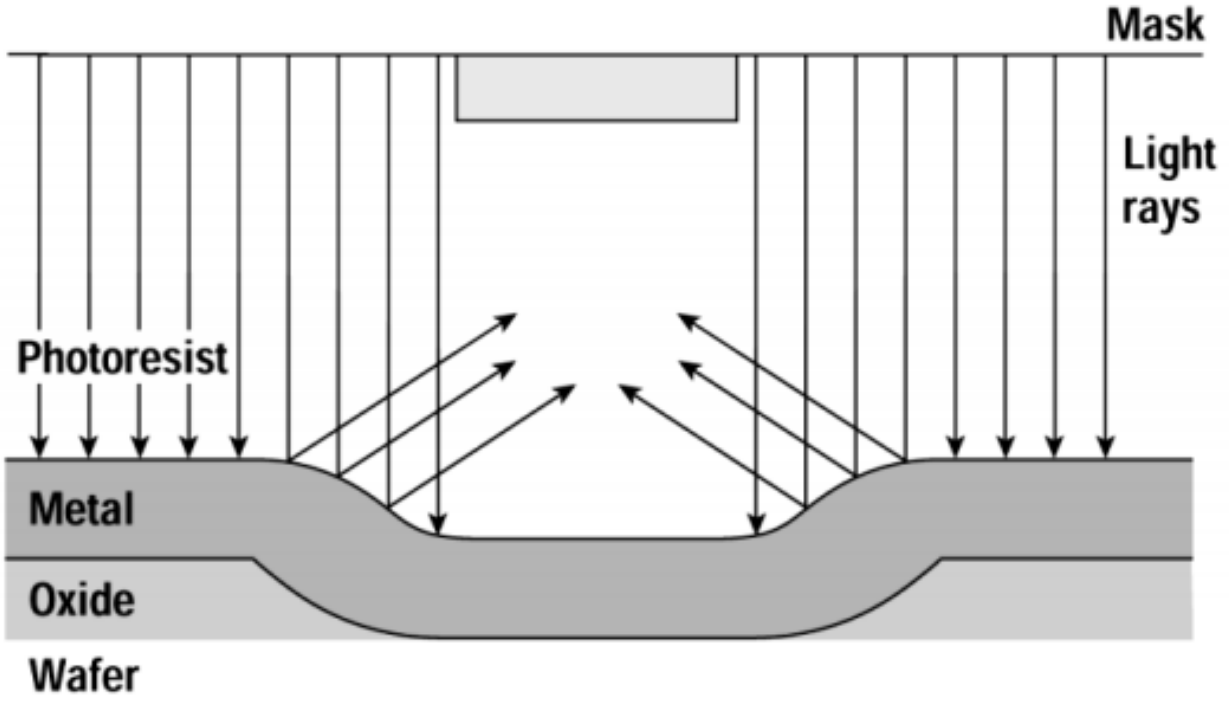


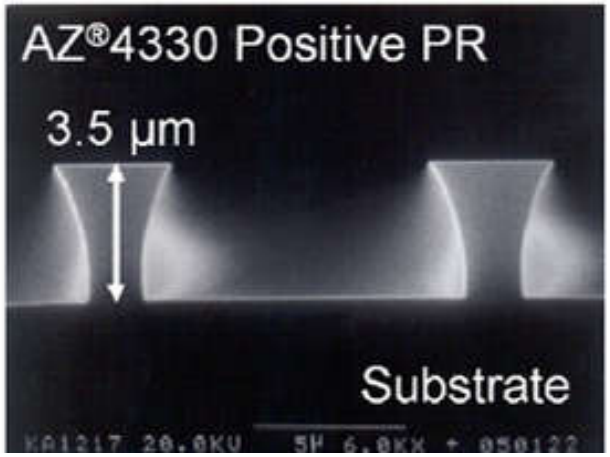


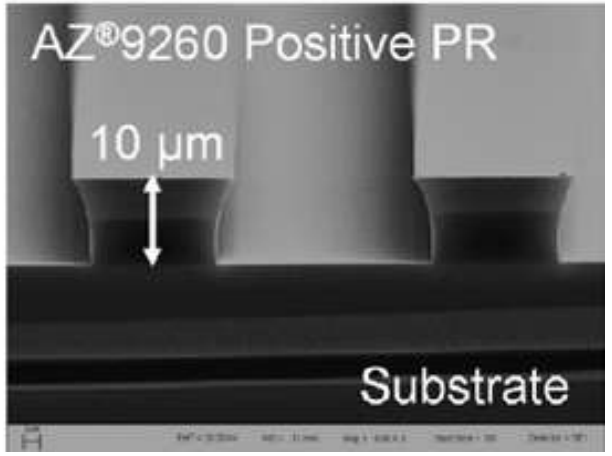




Proximity Scattering

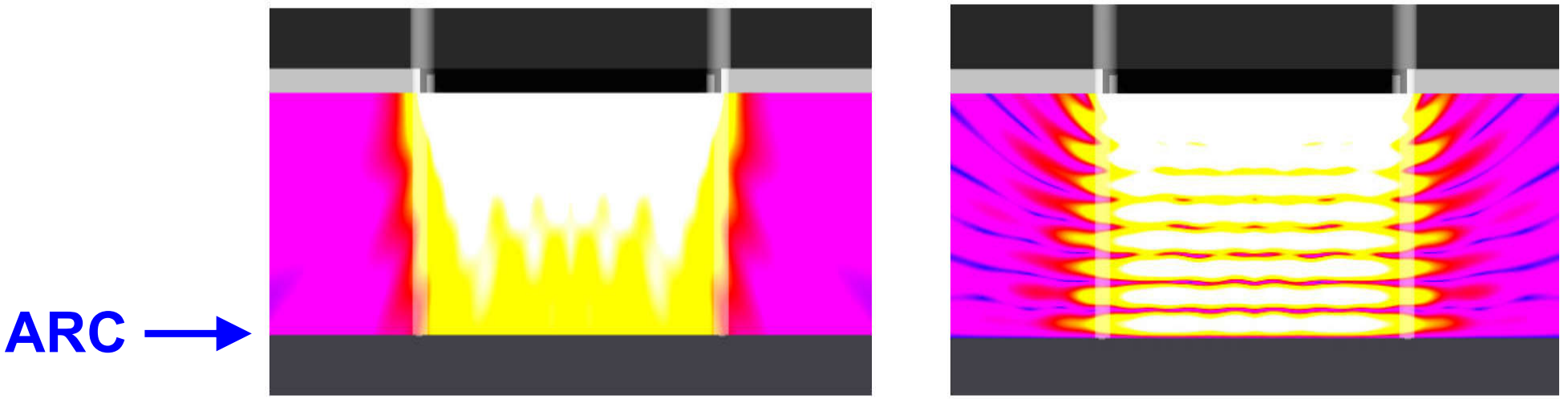






Reducing Substrate Effects

- Add absorptive dyes in photoresists
- Apply anti-reflective coatings (ARC)

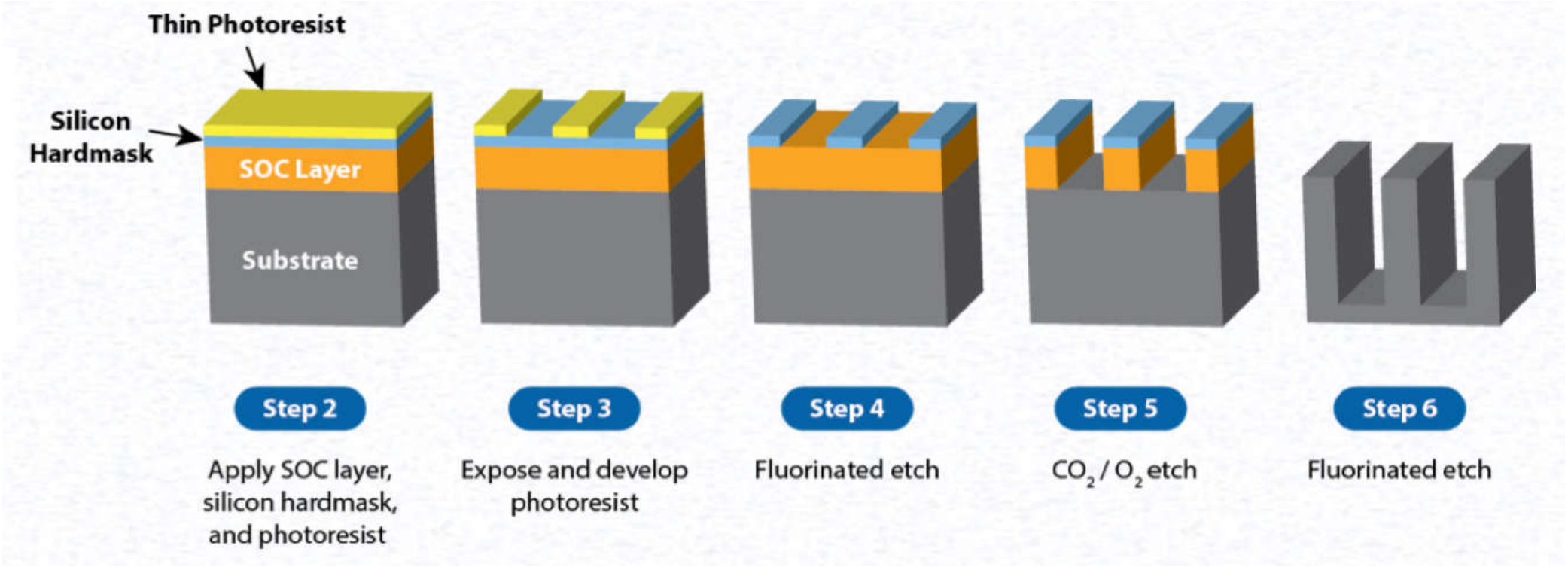


with ARC

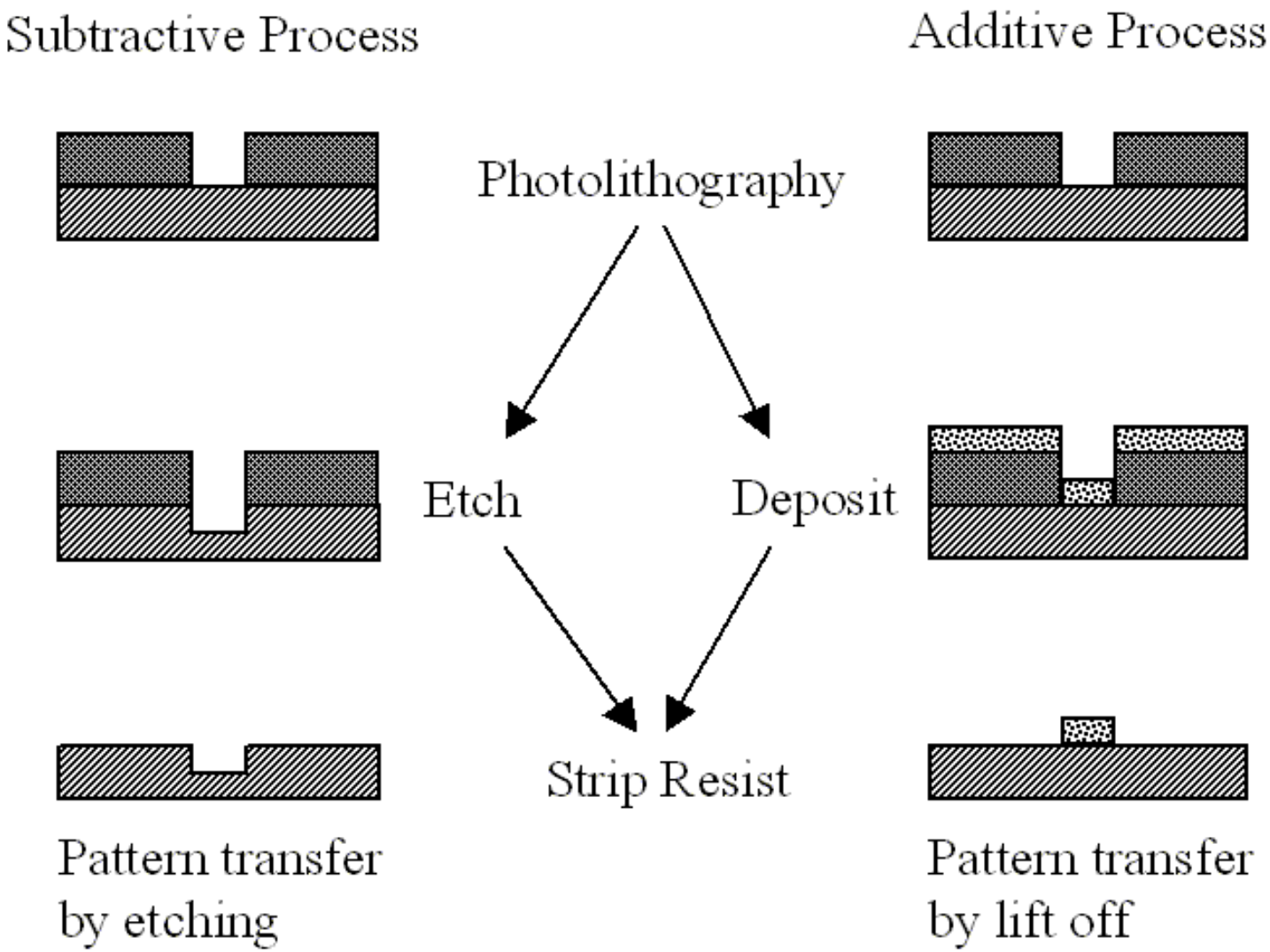
without ARC

Reducing Substrate Effects

- **Apply multilayer resists**



Pattern Transfer

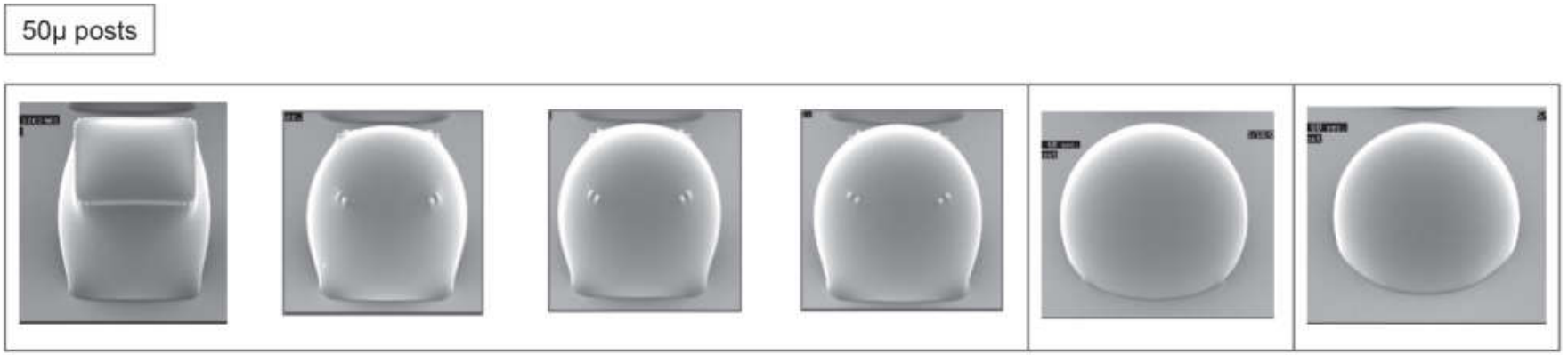


positive resist - etching

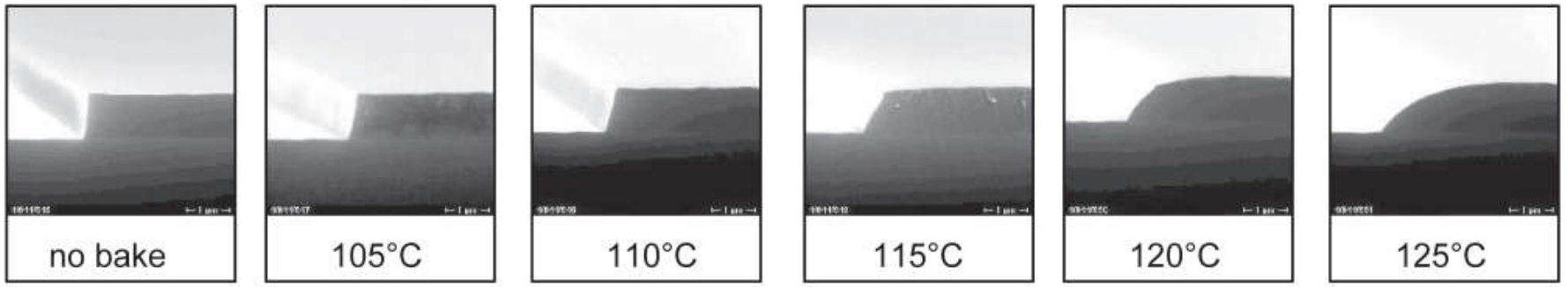
negative resist - liftoff

Photoresist Reflow

- **photoresists are soft polymers**
  - **flow at high temperature**



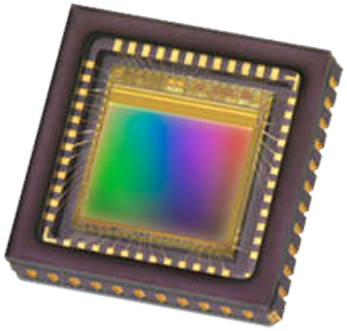
Reflow of AZ® 40 XT cubes at different temperatures and for different time. Images taken from the *AZ 40XT-11D Thermal Flow* data sheet of AZ-EM.

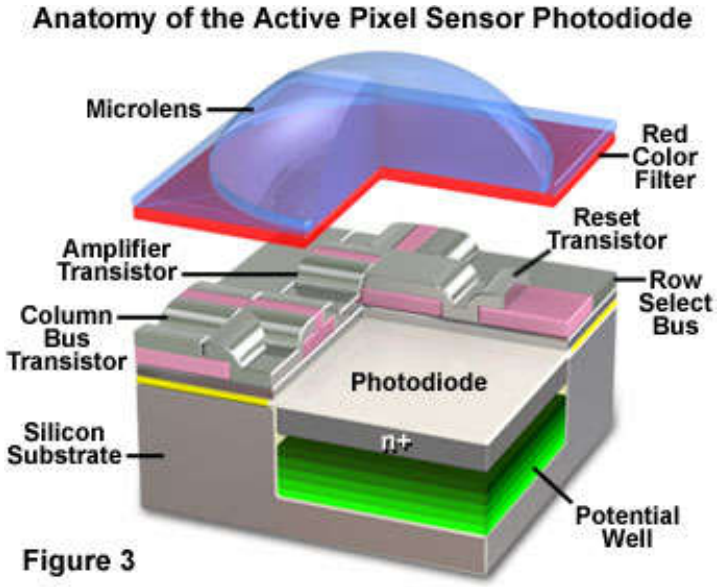


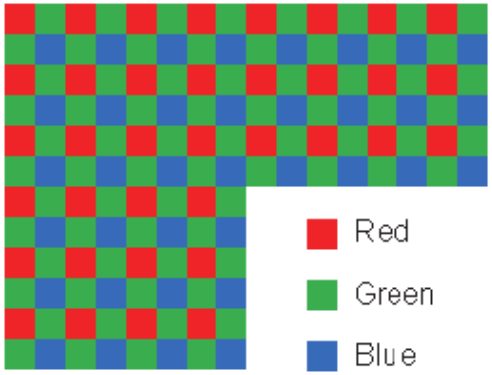
Photoresist Reflow

- **Microlens array by reflow**

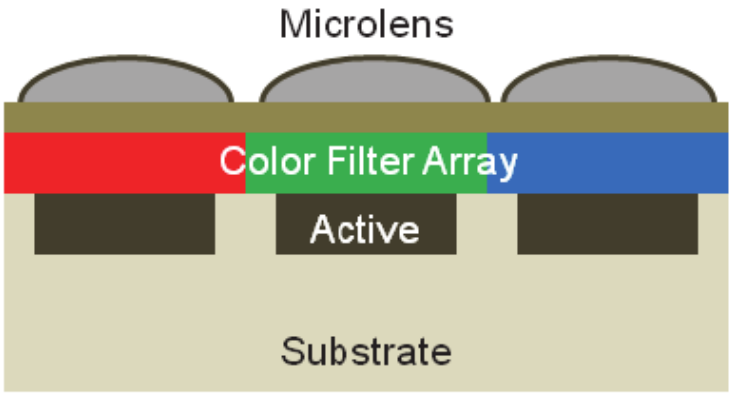
CMOS image sensor







Bayer Filter Pattern



Imager Photodiode cross-section

Photoresist Removal

- **Organic solvents**
  - acetone / isopropanol / DI water
  - NMP, DMSO, ...
- **Highly cross-linked resist cannot be removed by solvents**
- **Oxygen plasma**
  - polymer (C, H, O, ...) + O_2 = CO_2 + H_2O + ...

References for Photoresists

- **Useful notes for photolithography**

http://www.microchemicals.com/downloads/application_notes.html

- **Always read manuals before experiments**

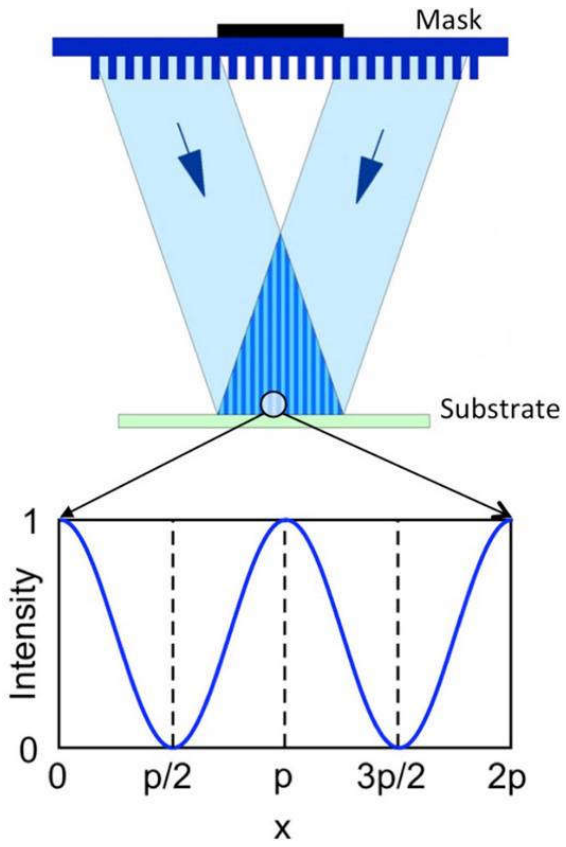
http://www.microchemicals.com/products/photoresists.html

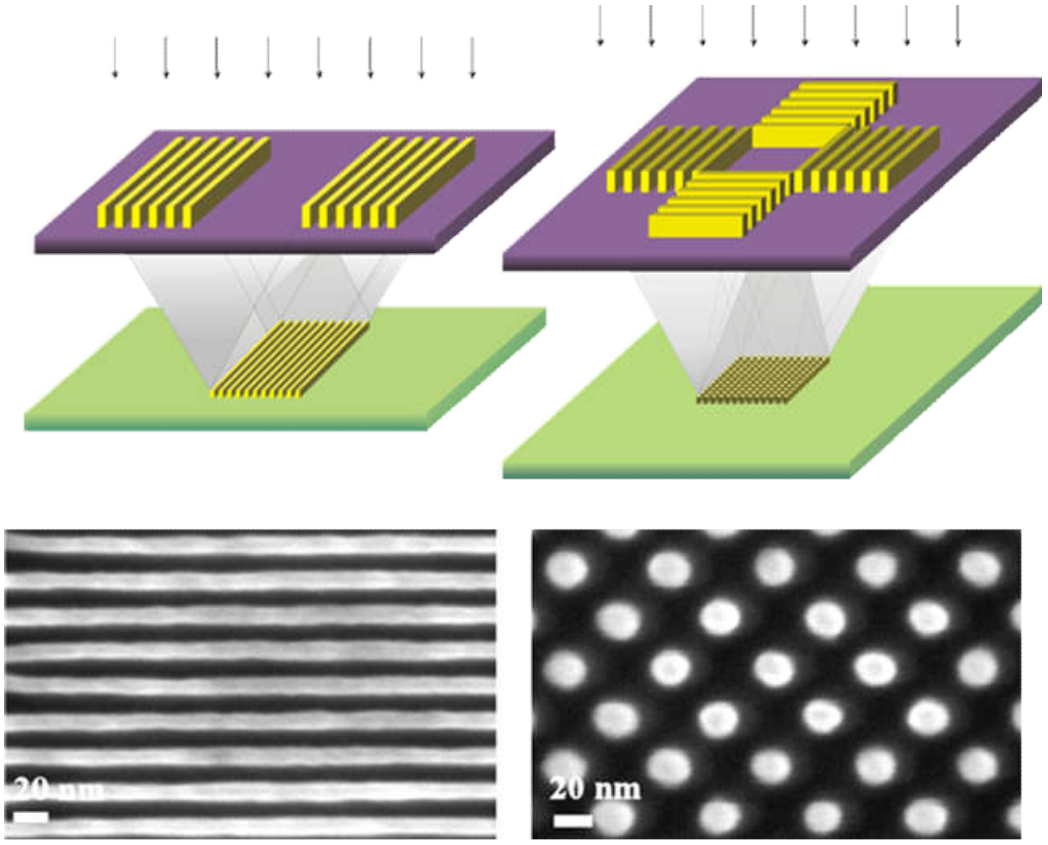
Advanced Lithography

- Interference / holographic lithography
- 3D lithography
- Plasmonic lithography
- Nanoimprint lithography
- Directed self-assembly lithography
- Inorganic materials based lithography

Interference / Holographic Lithography

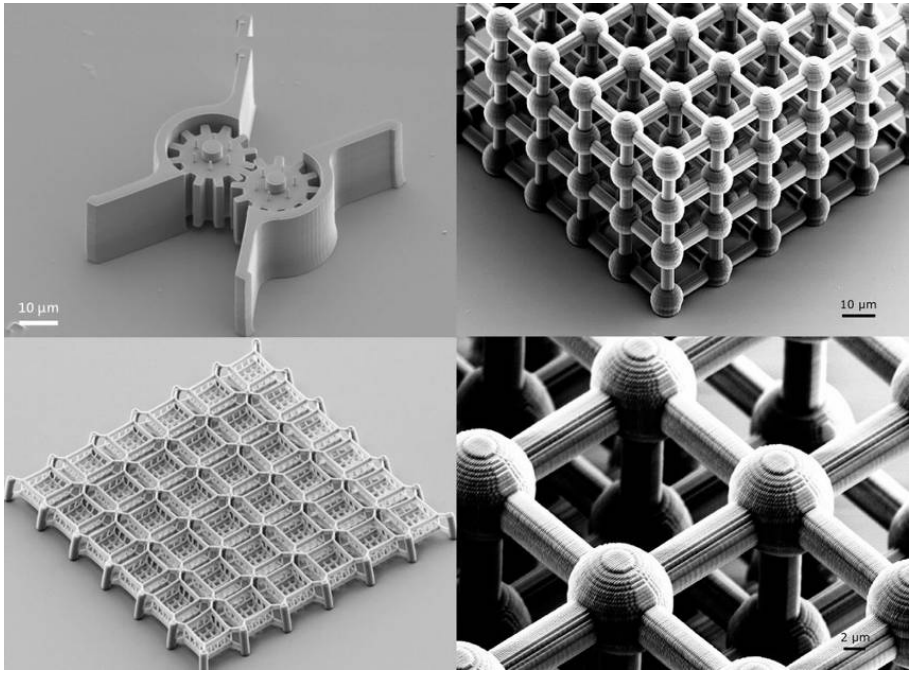
- **resolution ~ λ/2**
  - **easy to form periodic patterns**

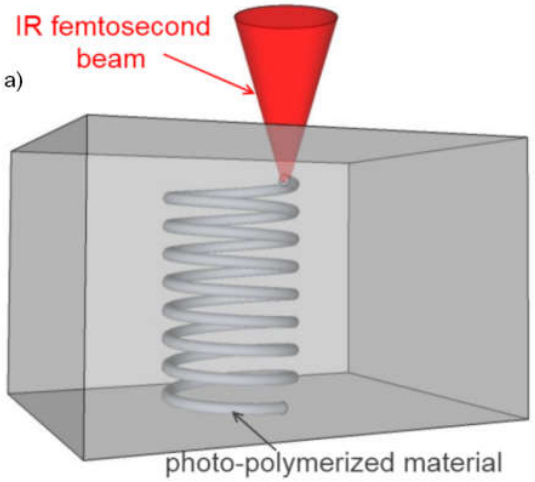


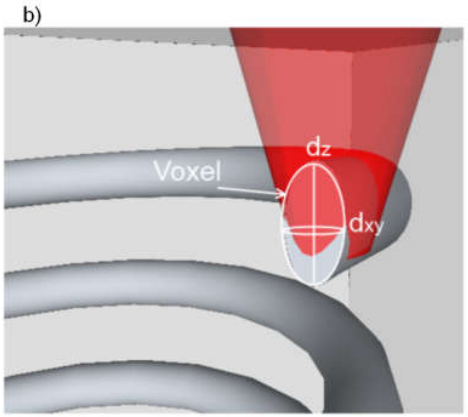


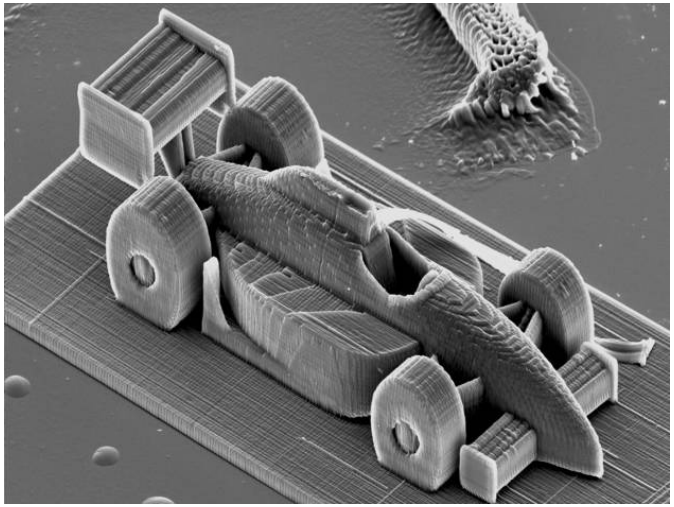
3D Lithography

- direct laser writing
  - two photon absorption







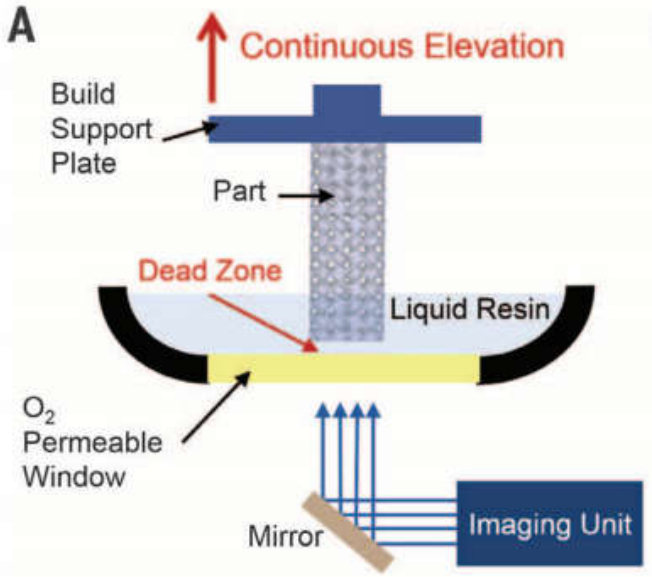


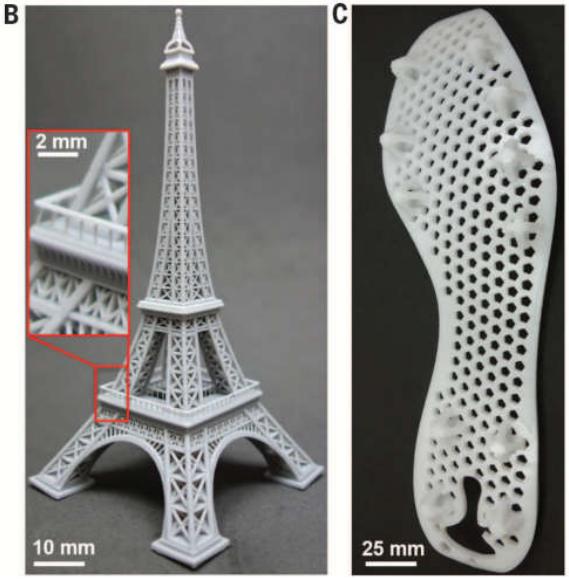
3D Lithography

ADDITIVE MANUFACTURING

Continuous liquid interface production of 3D objects

John R. Tumbleston,[1] David Shirvanyants,[1] Nikita Ermoshkin,[1] Rima Janusziewicz,[2] Ashley R. Johnson,[3] David Kelly,[1] Kai Chen,[1] Robert Pinschmidt,[1] Jason P. Rolland,[1] Alexander Ermoshkin,[1*] Edward T. Samulski,[1,2*] Joseph M. DeSimone[1,2,4*]

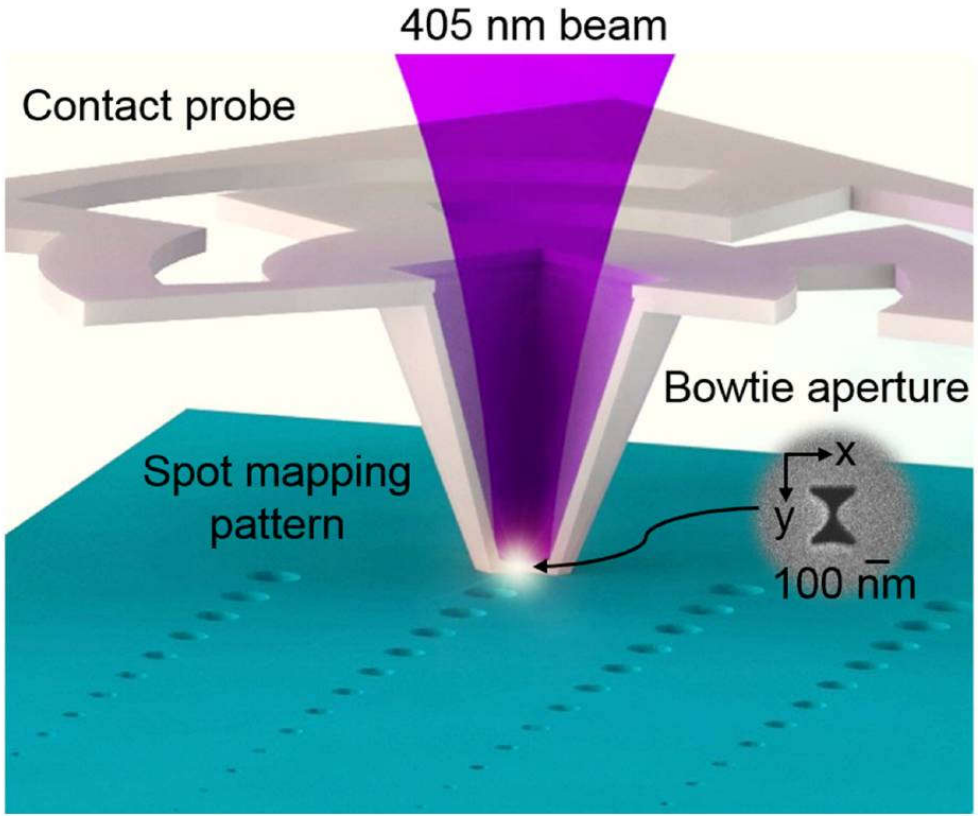




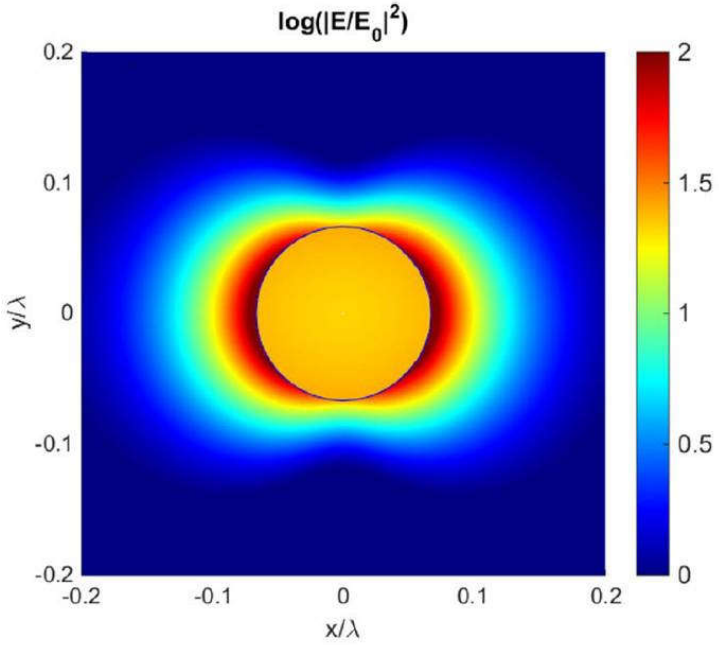
Video

J. R. Tumbleston, *et al.*, *Science* **347,** 1349 (2015)

Plasmonic Lithography



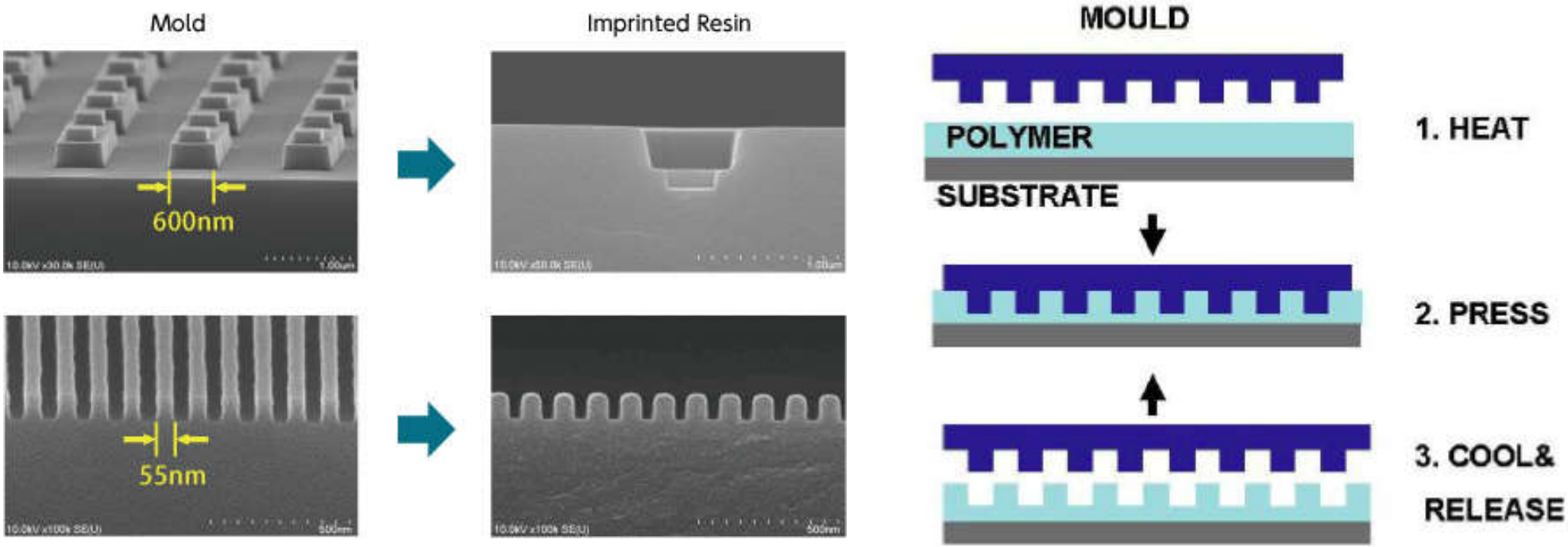
subwavelength resolution



field enhancement at metal surfaces

Nanoimprint Lithography

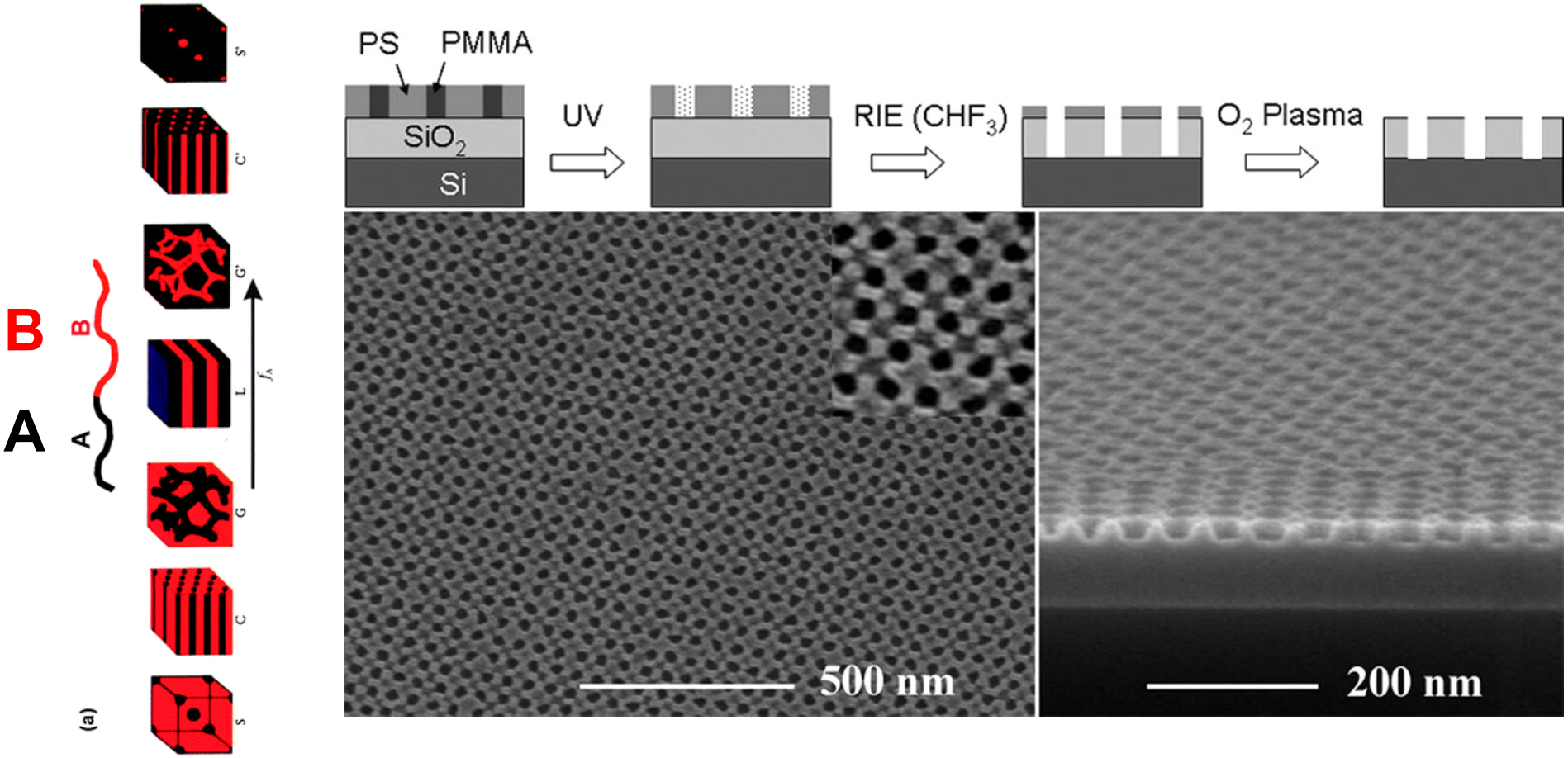
- **Nanoscale mold fabricated by advanced lithography**
  - **silicon, etc.**
  - **reusable**



S. Y. Chou, et al., *Science* **272,** 5258 (1996)

Direct Self-assembly

- **Phase separation by block copolymers**



C. Tang, et al., *Science* **322,** 429 (2008)

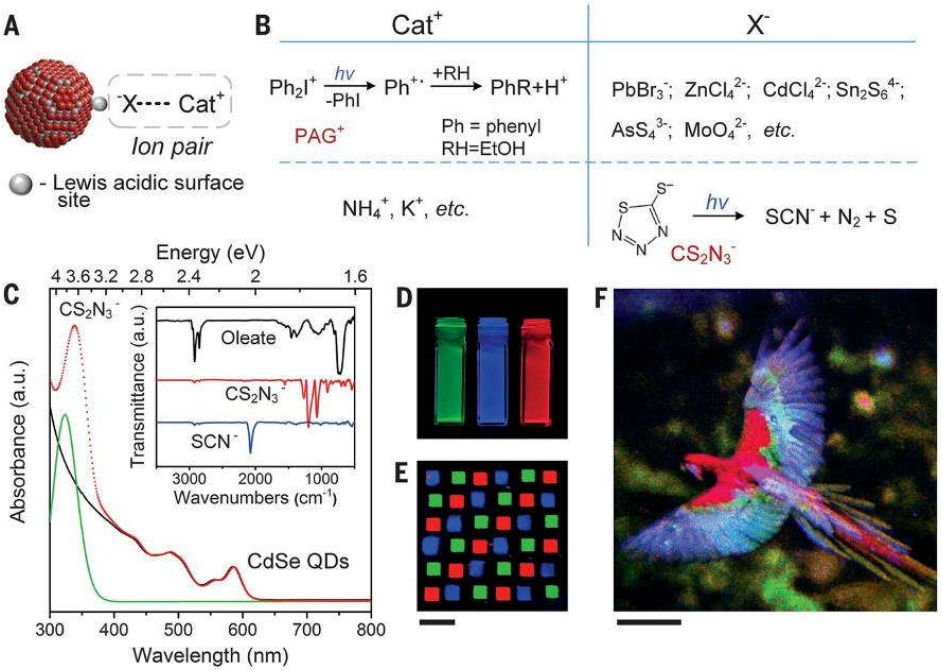
Lithography of Inorganic Materials

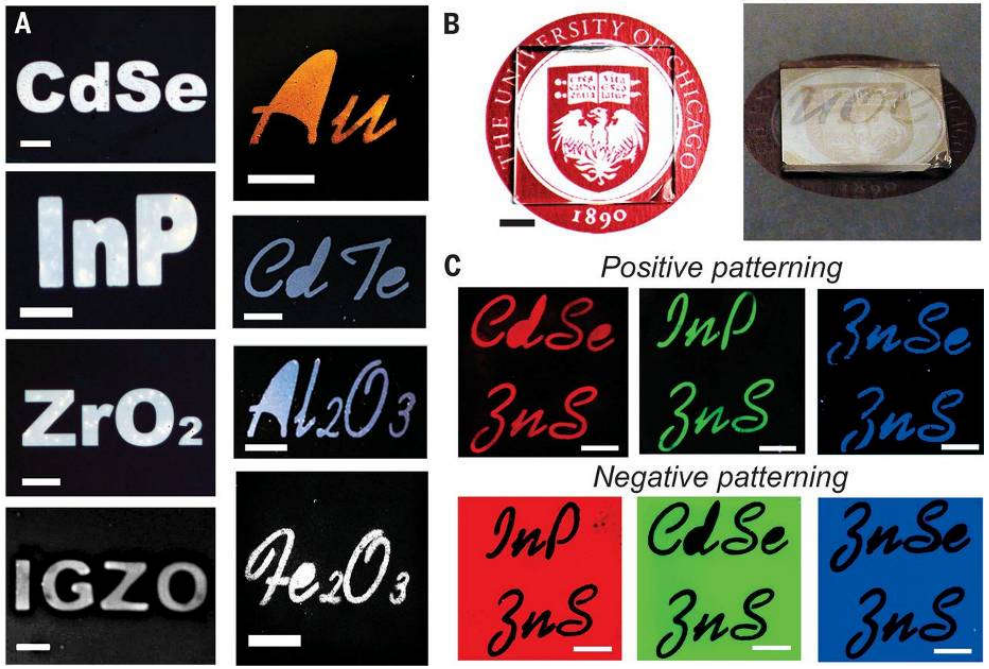
RESEARCH

LITHOGRAPHY

Direct optical lithography of functional inorganic nanomaterials

Yuanyuan Wang,[1,2] Igor Fedin,[1,2] Hao Zhang,[1,2] Dmitri V. Talapin[1,2,3]*





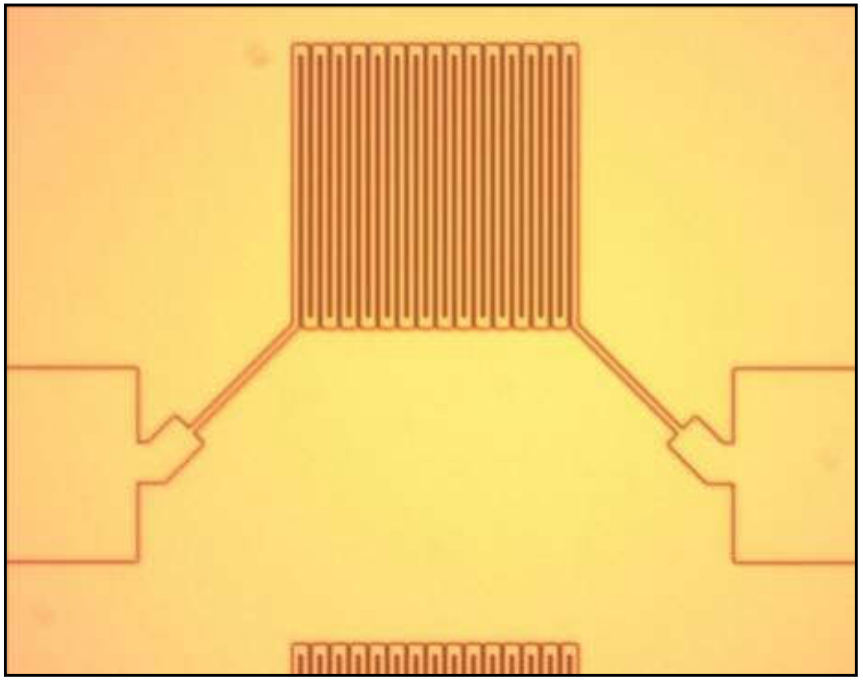
Y. Wang, et al., *Science* **357,** 385 (2017)

Metrology

- Optical microscope
- Profilometer (non-contact)
- Profilometer (contact)
- Atomic force microscope (AFM)
- Electron microscopy (SEM, TEM, cryo-EM)
- Scanning tunneling microscope (STM)

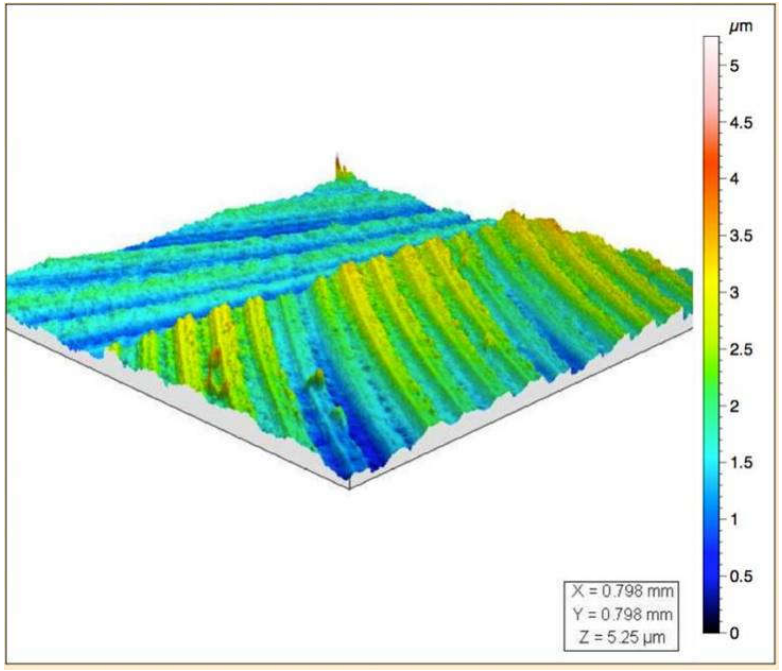
Metrology

- **Optical microscope**
  - use yellow filter to prevent resist exposure
  - resolution determined by optics



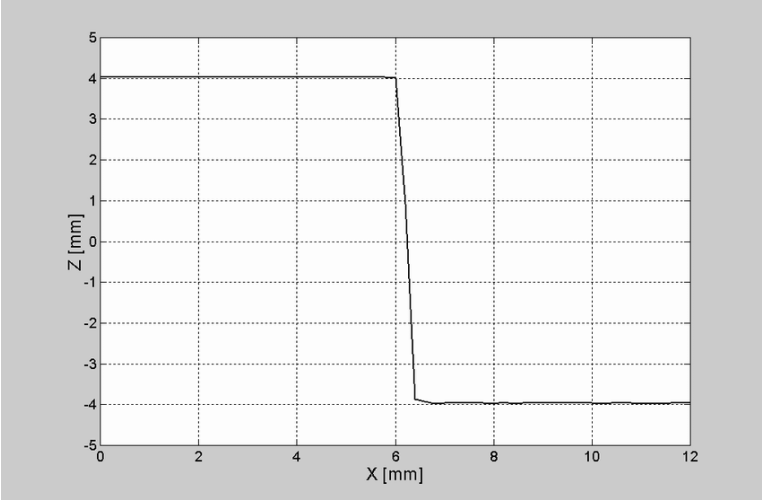
Metrology

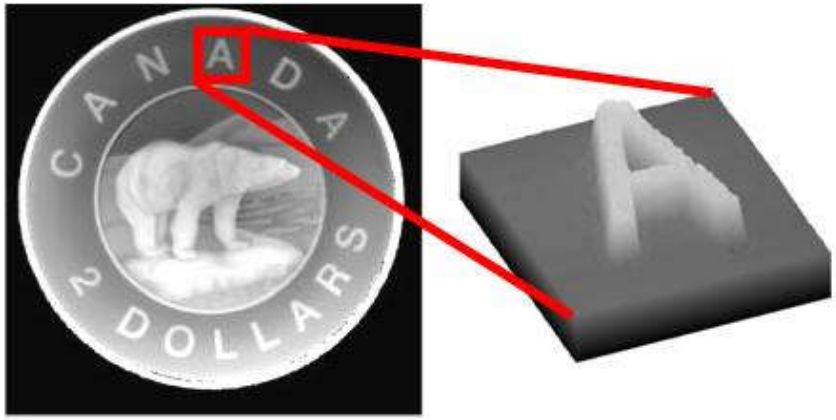
- **Profilometer (non-contact)**
  - optical scanning
  - measure 3D profile
  - spatial resolution - wavelength
  - not suitable for absorptive materials



Metrology

- **Profilometer (contact)**
  - stylus
  - measure film thickness
  - 2D or 3D profile
  - spatial resolution - stylus





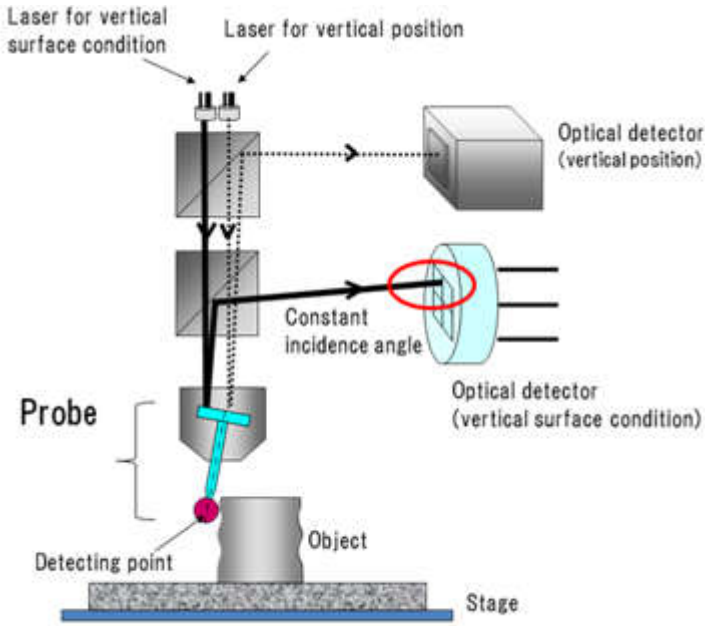
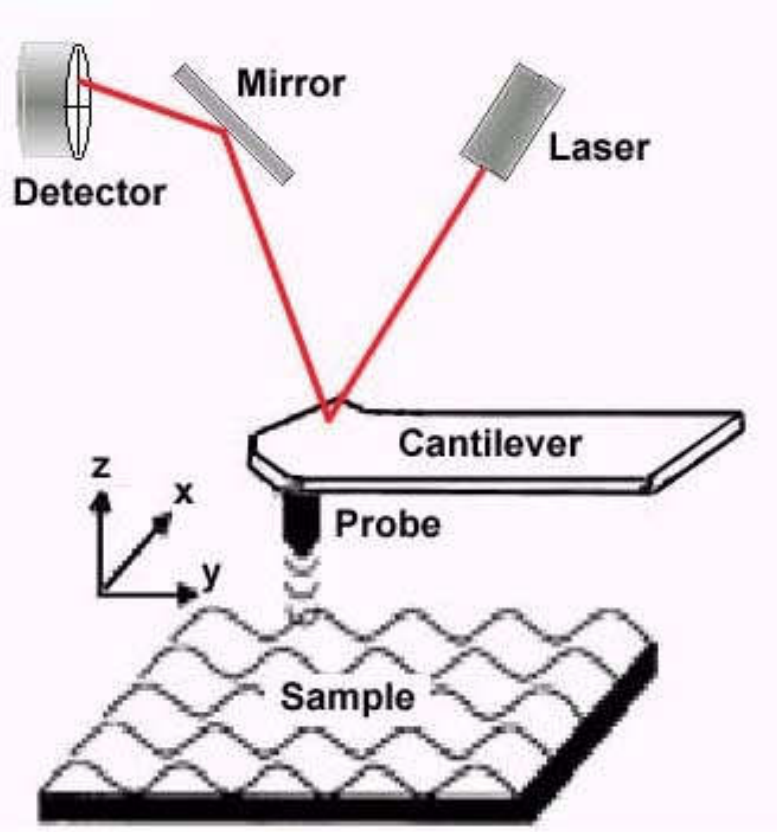
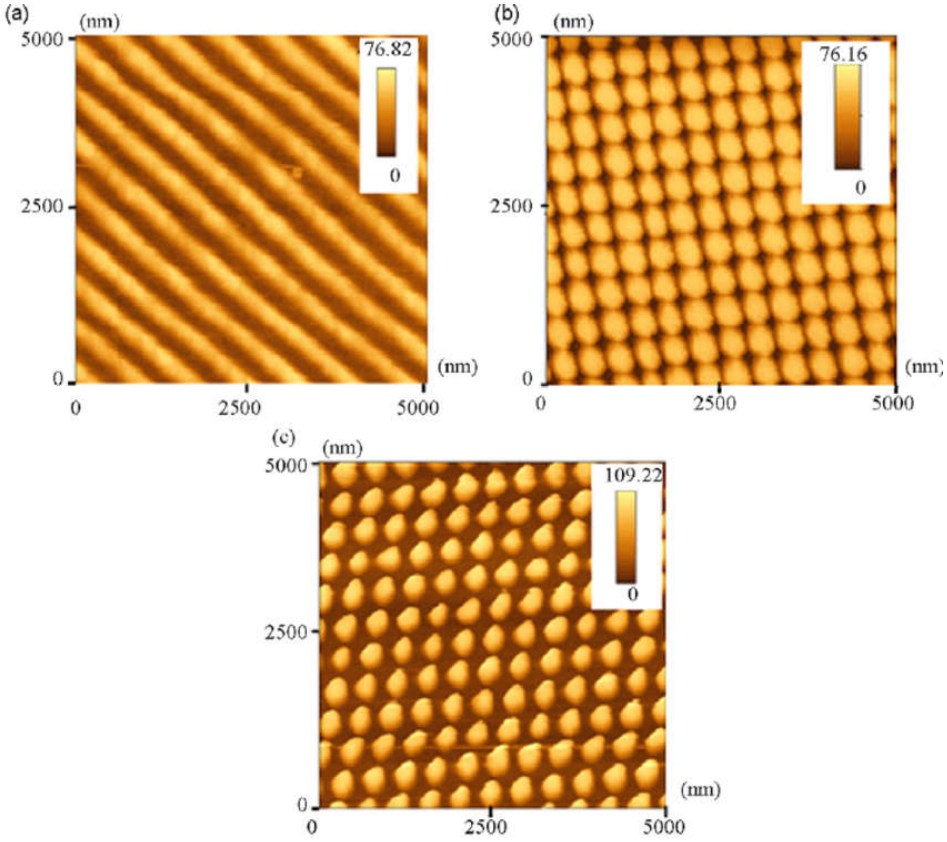


Fig.1 Optical System in Ultrahigh Accurate 3D Profilometer

Metrology

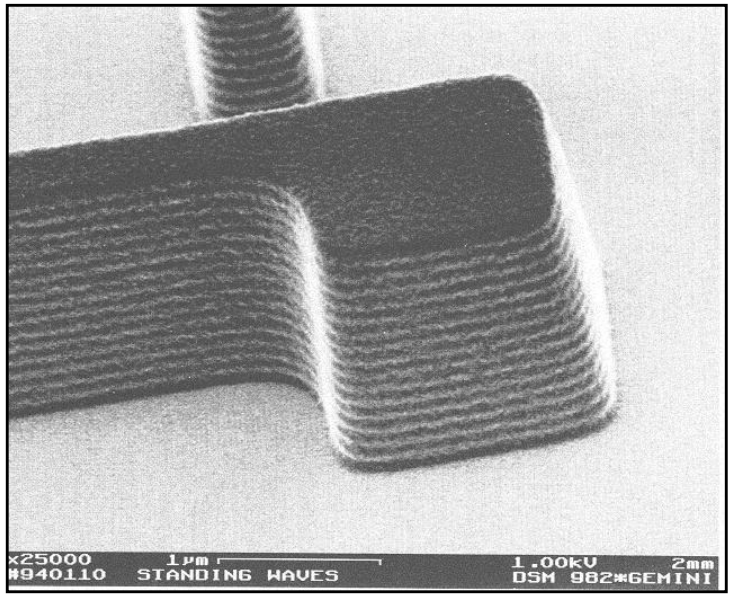
- **Atomic force microscope (AFM)**
  - **better horizontal and vertical resolution**

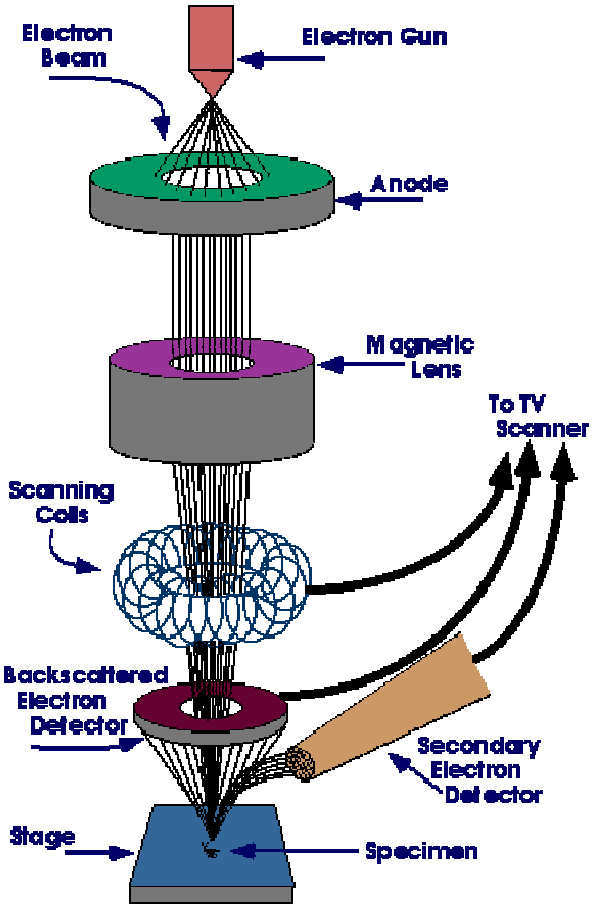




Metrology

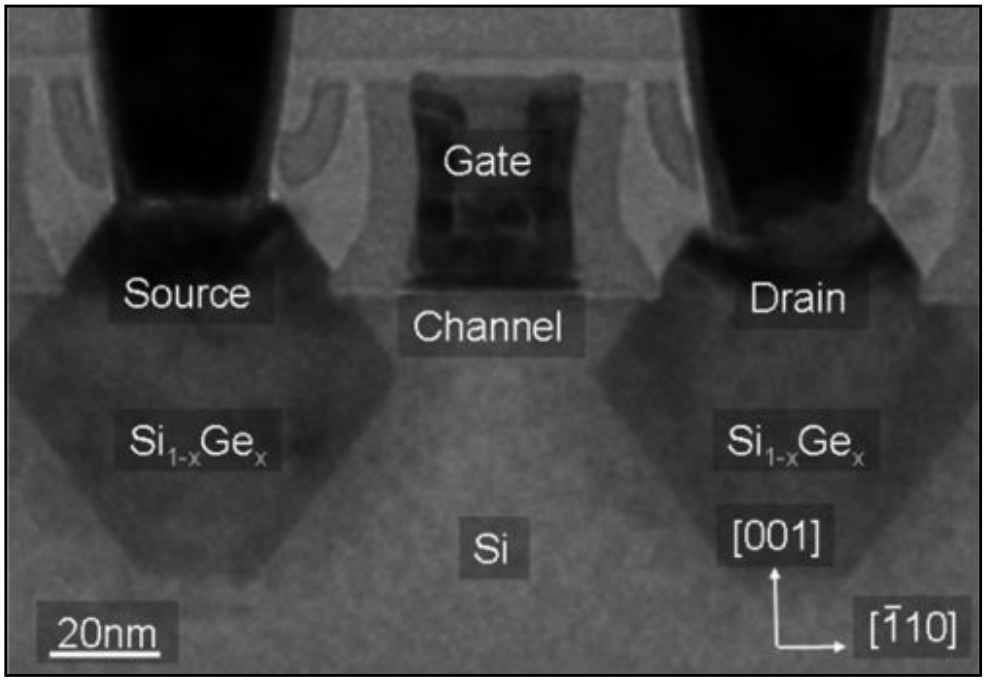
- Scanning electron microscope (SEM)
  - vacuum required
  - surface charging
  - can combine with Ebeam lithography

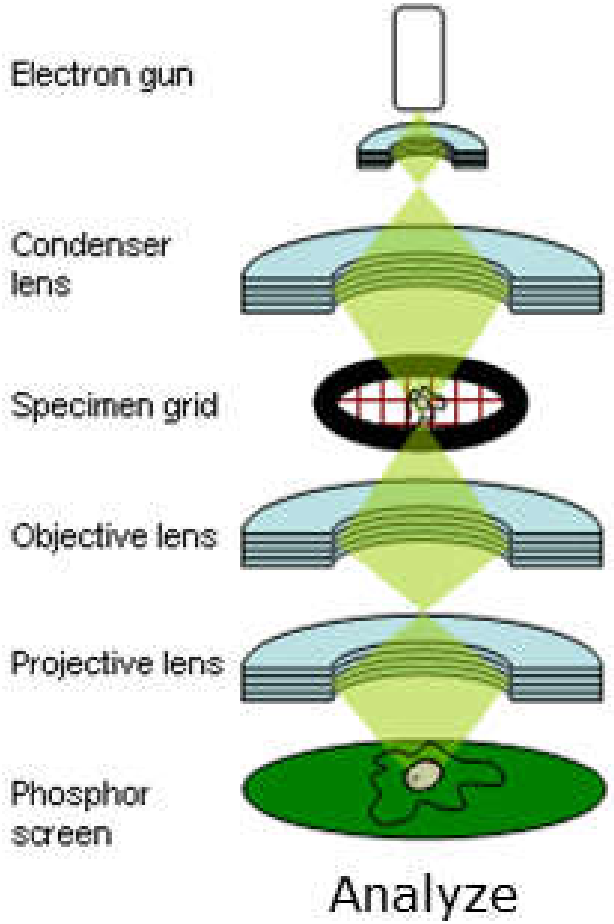




Metrology

- transmission electron microscope (TEM)
  - higher resolution than SEM
  - thin samples



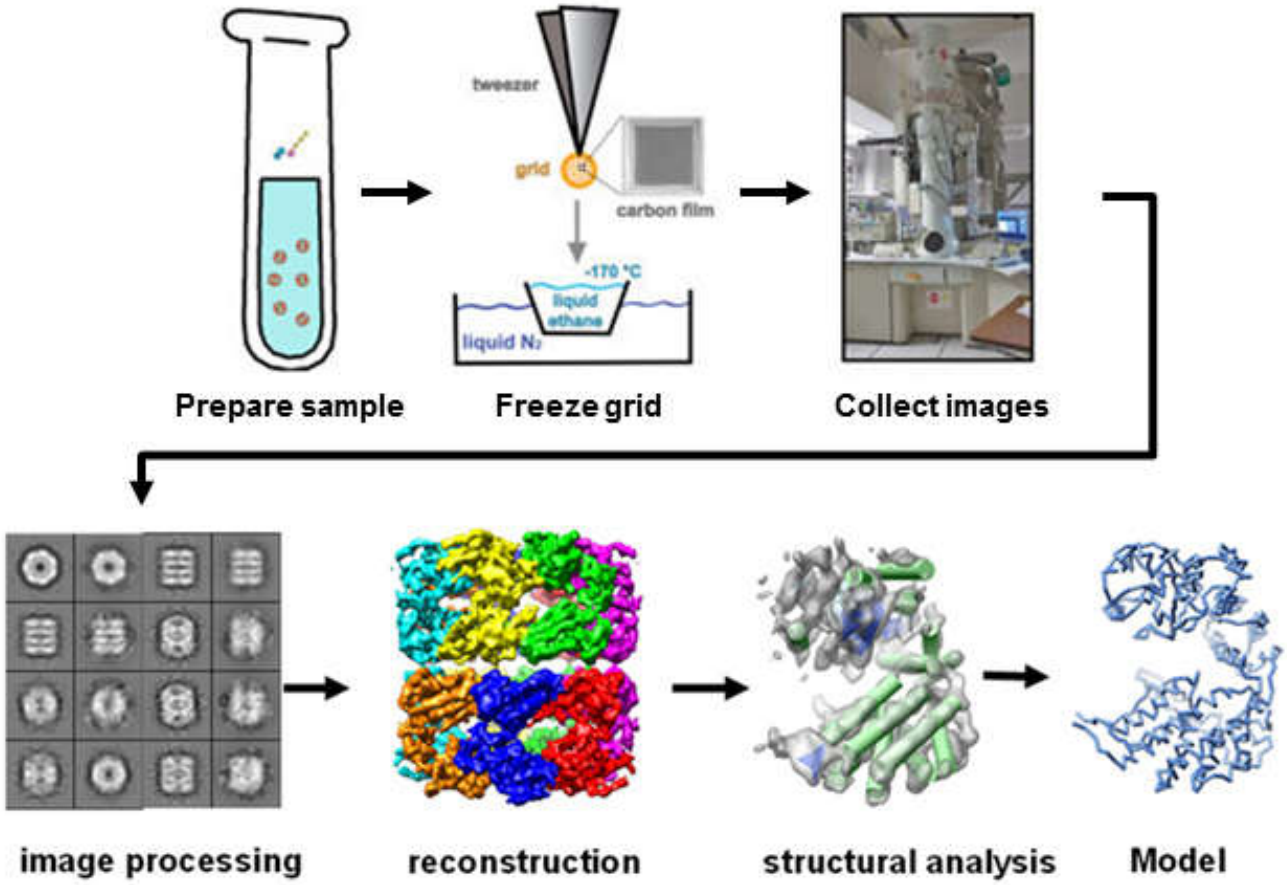


A. Klug
1982 Nobel Prize in Chemistry

E. Ruska
1986 Nobel Prize in Physics

Metrology

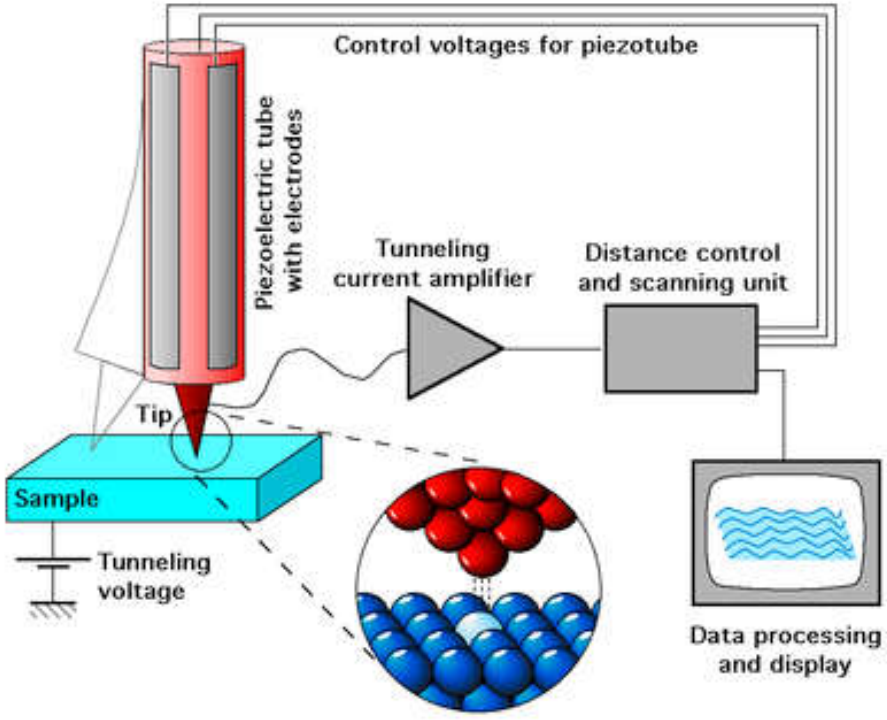
- cryo electron microscope (cryo-EM)
  - image biological samples!



2017 Nobel Prize in Chemistry

Metrology

- Scanning tunneling microscope (STM)
  - atomic resolution
  - ultrahigh vaccum
  - image and manipulate atoms



G. Binnig, H. Rohrer
1986 Nobel Prize in Physics

Thank you for your attention