Principles of Micro- and Nanofabrication for Electronic and Photonic Devices

Photolithography 光刻

Part II: Photoresists

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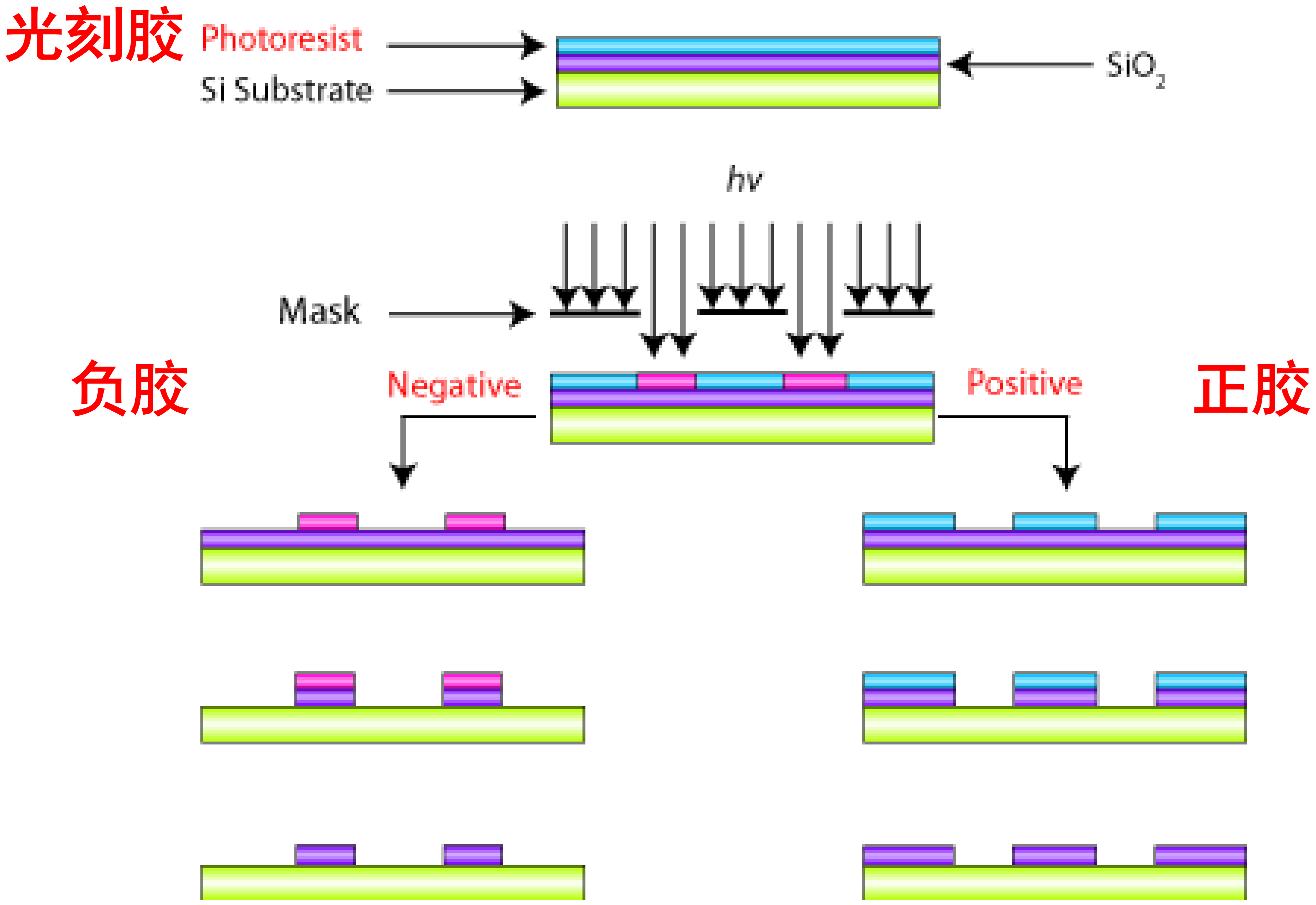
Photolithography



Photolithography

Dark room

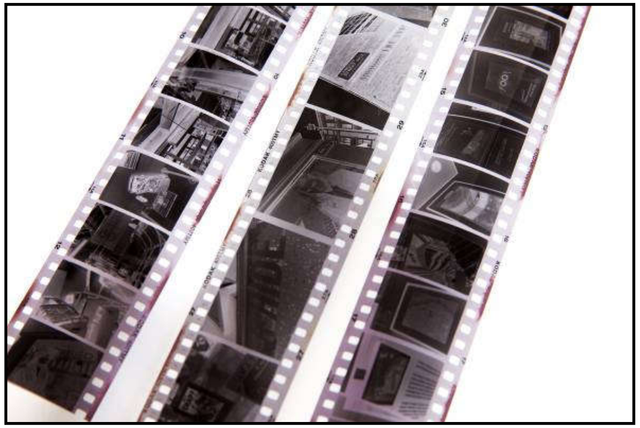
photography

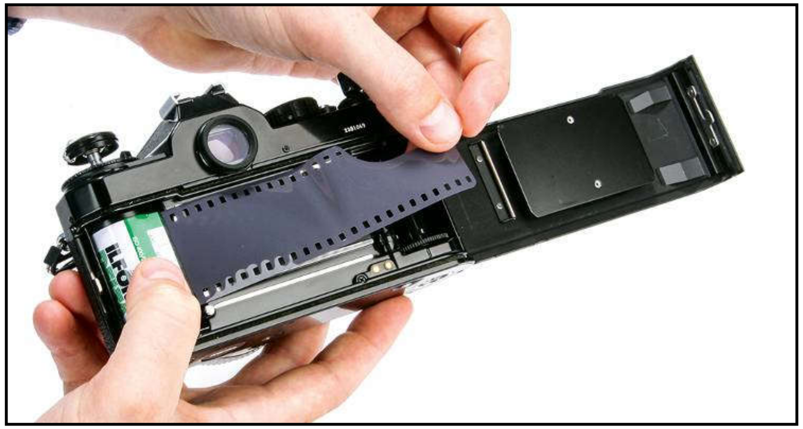
Yellow zone

avoid UV exposure!

Photography

$$AgBr = Ag + Br_2$$

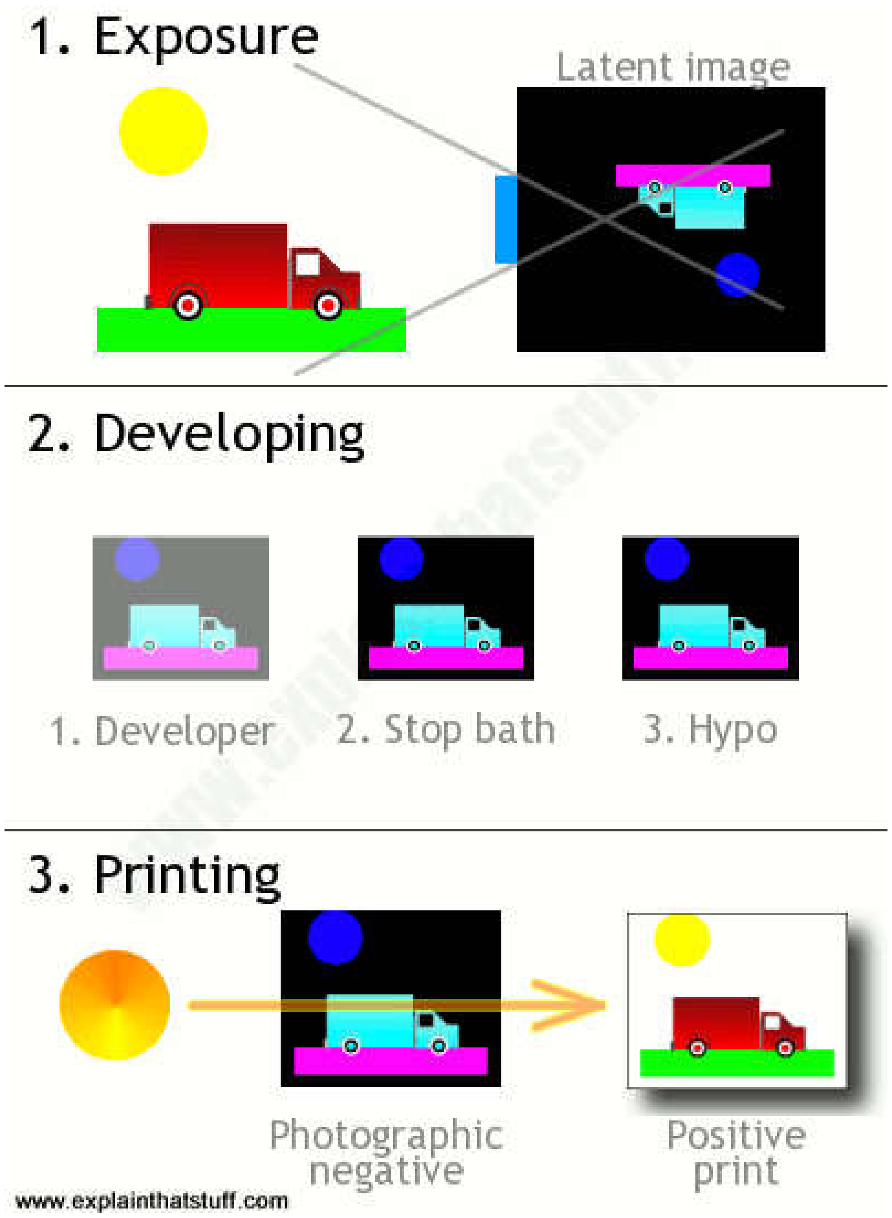




曝光

显影

打印



Photolithography

Sample clean

Surface treatment

Photoresist coating

Prebake

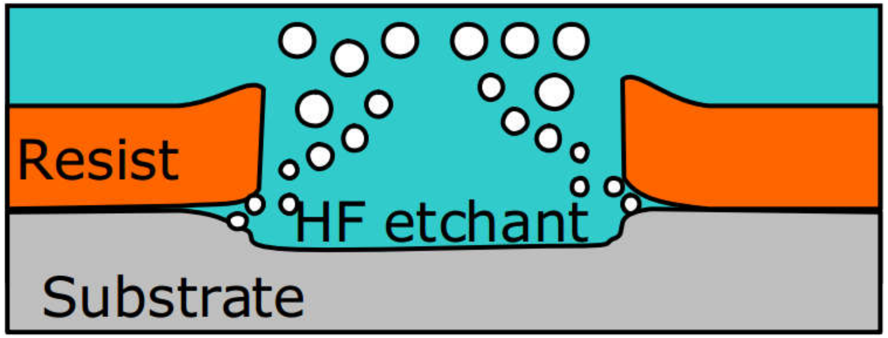
Exposure

Postexposure bake

Development

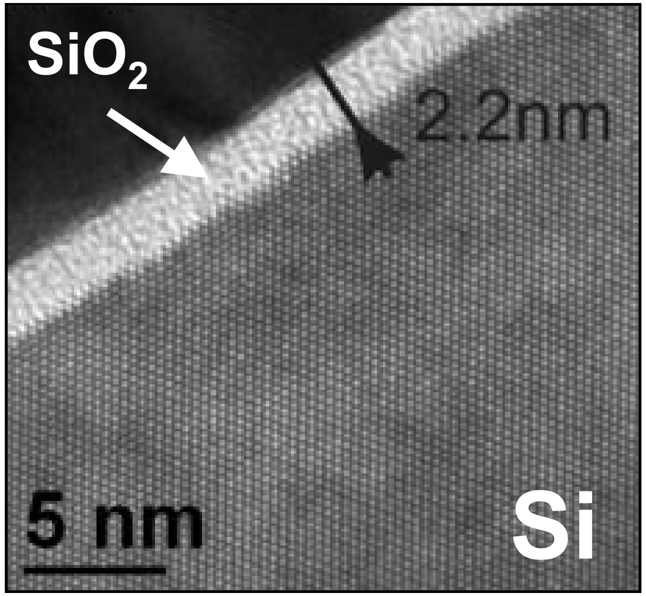
Photoresist Adhesion: Issues

- 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, ...

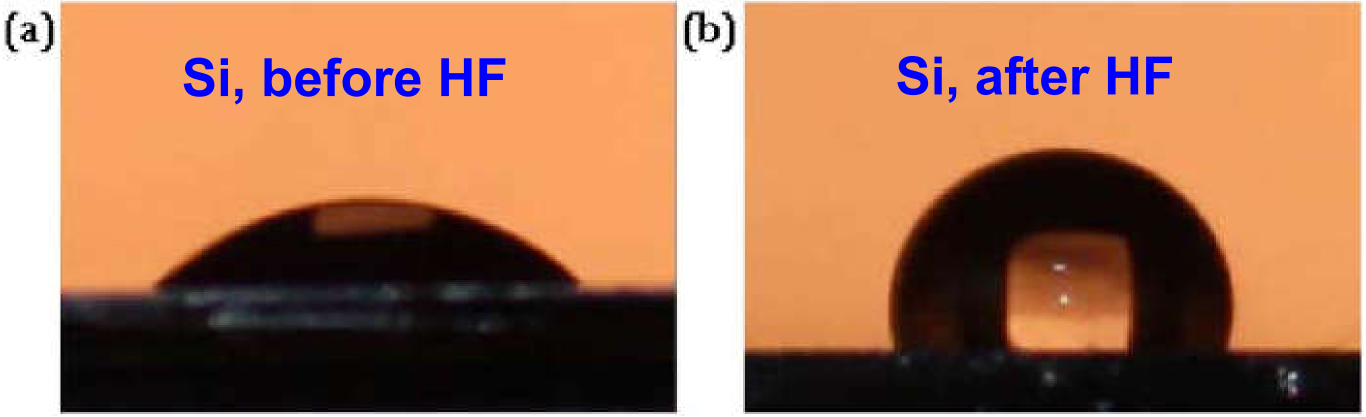


Photoresist Adhesion: Solutions

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



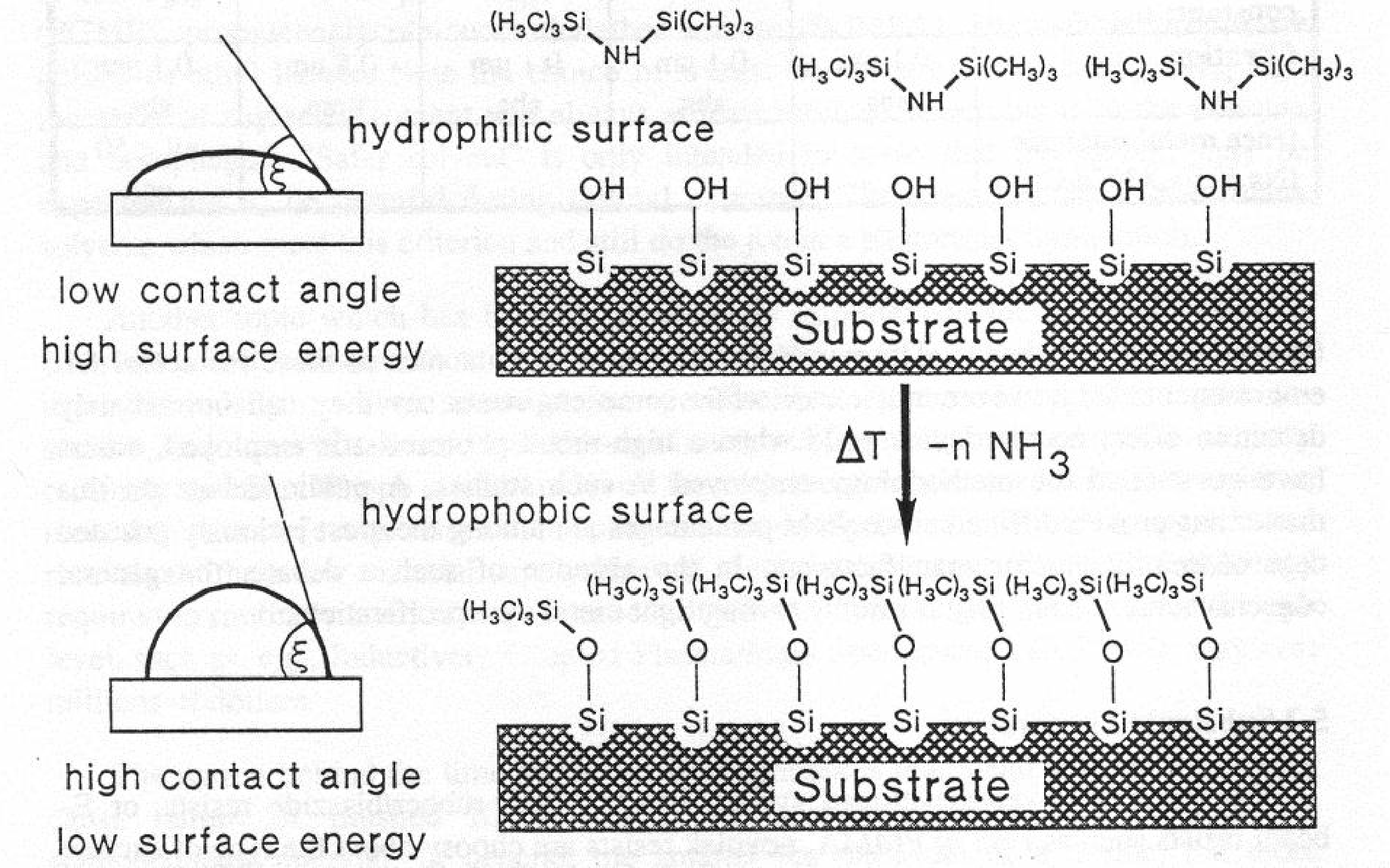
- **Dehydration bake**
  - remove water from sample surface



Q: Why?

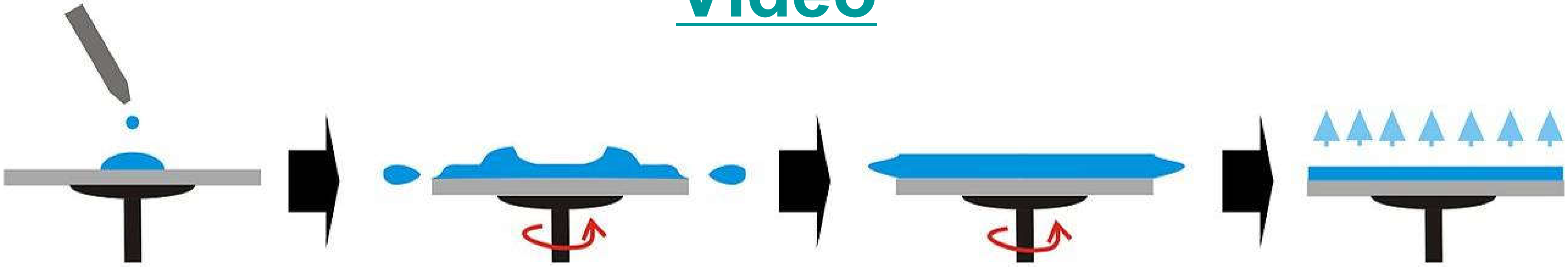
Photoresist Adhesion: Solutions

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



Spin Coating

Video



thickness

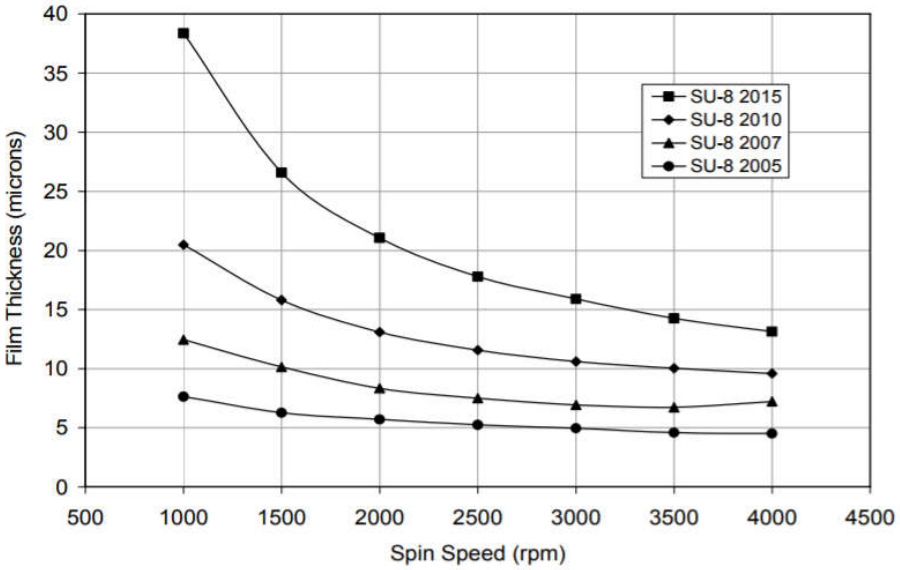
$$\boxed{h \sim \left(\frac{\mu}{t\omega^2}\right)^{1/2}}$$

h	thickness
μ	viscosity
t	time
ω	speed

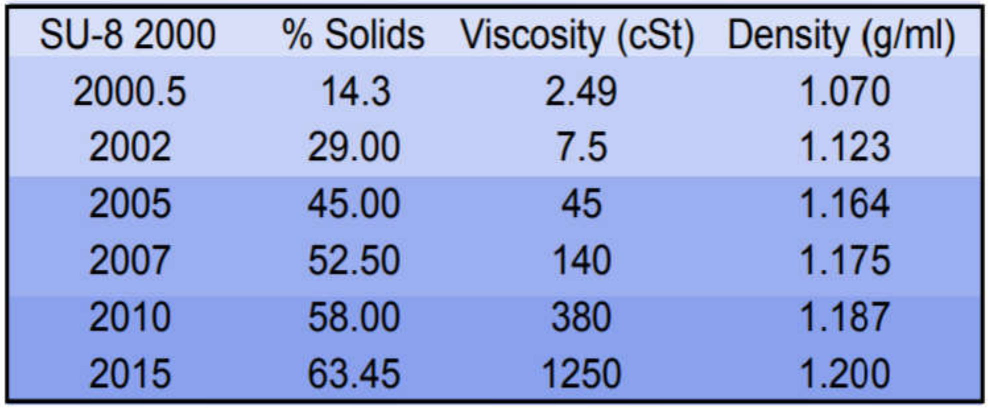
https://www.ossila.com/pages/spin-coating

Spin Coating – Film Thickness

thickness vs. speed and viscosity



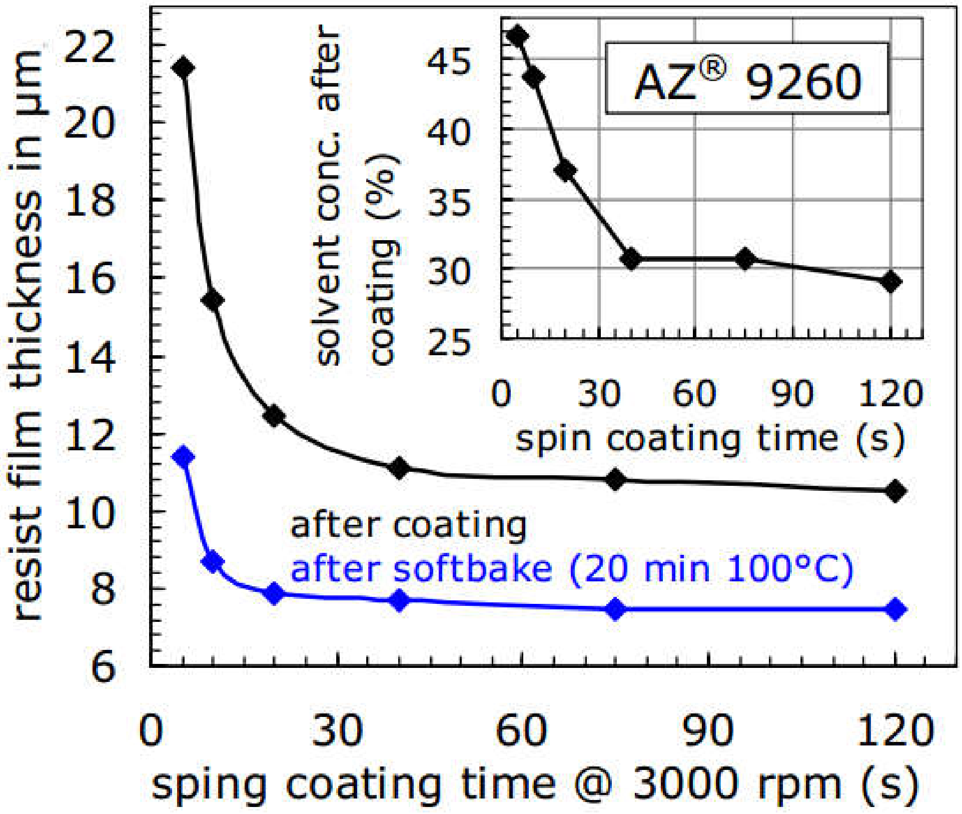
$$\boxed{h \sim \left(\frac{\mu}{t\omega^2}\right)^{1/2}}$$



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

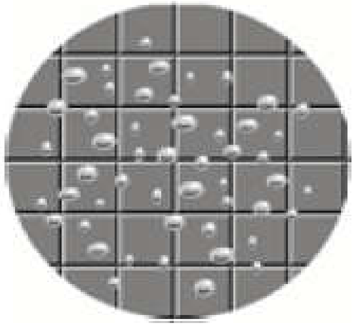
Spin Coating – Film Thickness

thickness vs. spin time

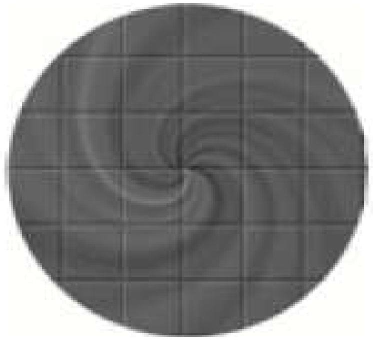


$$\boxed{h \sim \left(\frac{\mu}{t\omega^2}\right)^{1/2}}$$

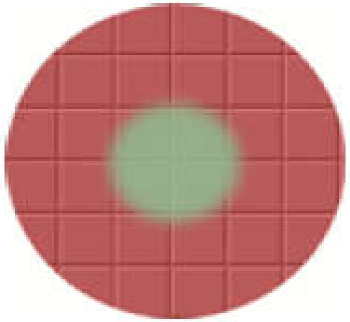
Spin Coating - Troubleshooting



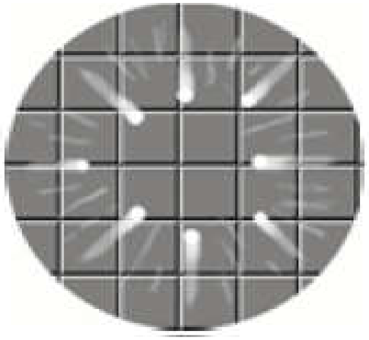
- bubbles in resist
- sample not clean
- N_2 generation



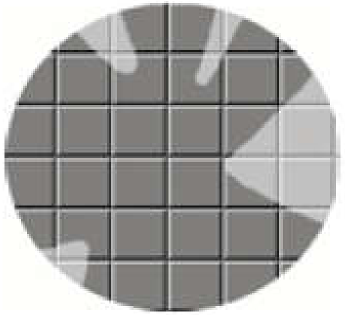
- accelerate too fast
- sample off center
- time too short
- evaporate too fast



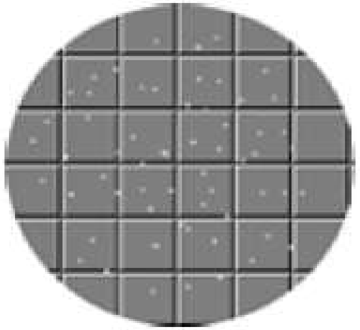
- improper chuck
- sample off center



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



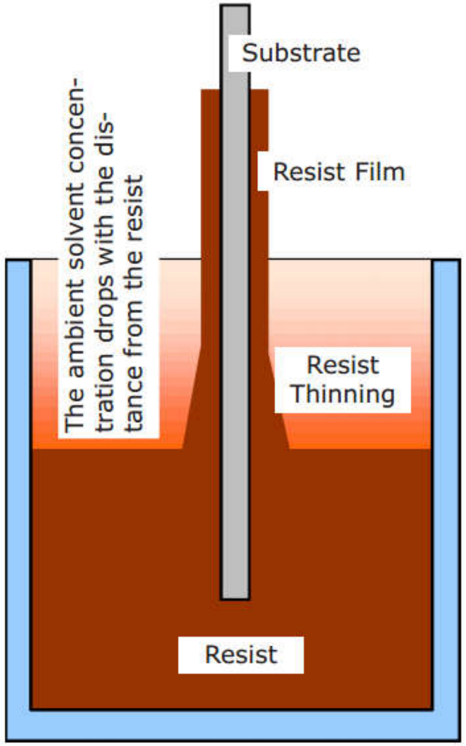
- fluid too little
- sample dewet
- sample not clean



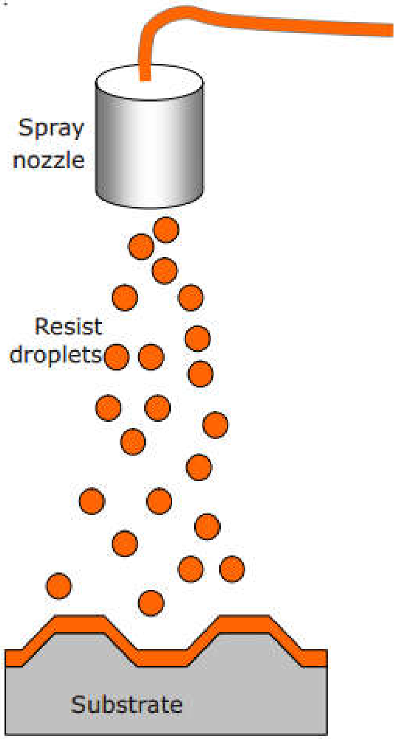
- sample not clean
- resist not clean

Other Coating Methods

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



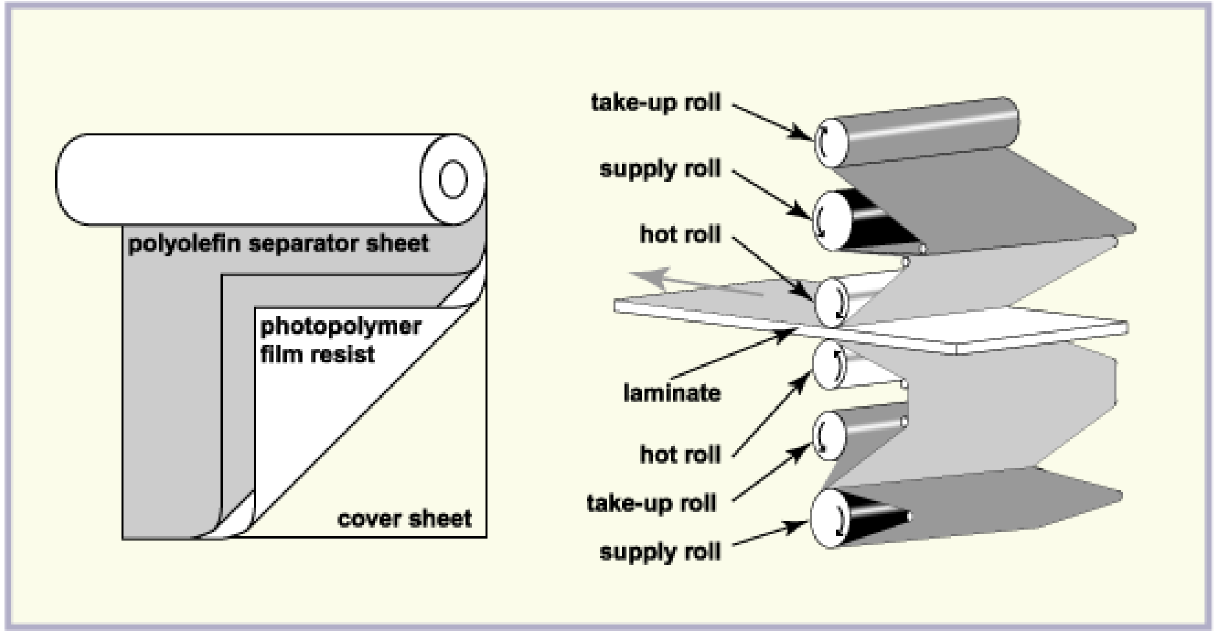
dip coating

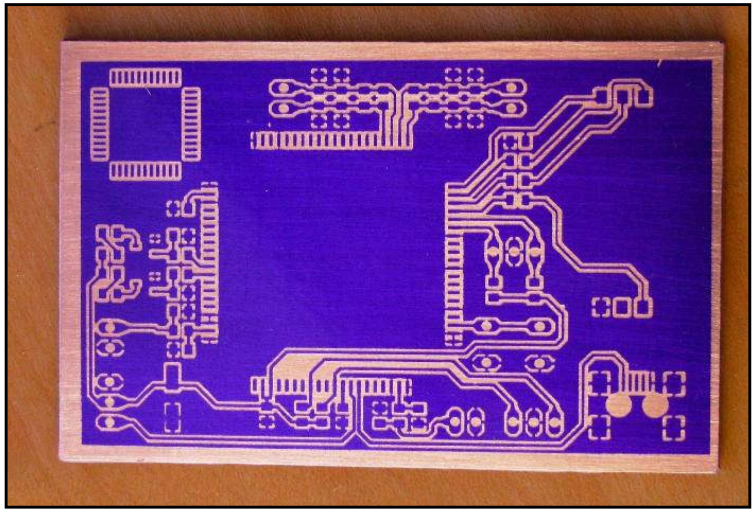


spray coating

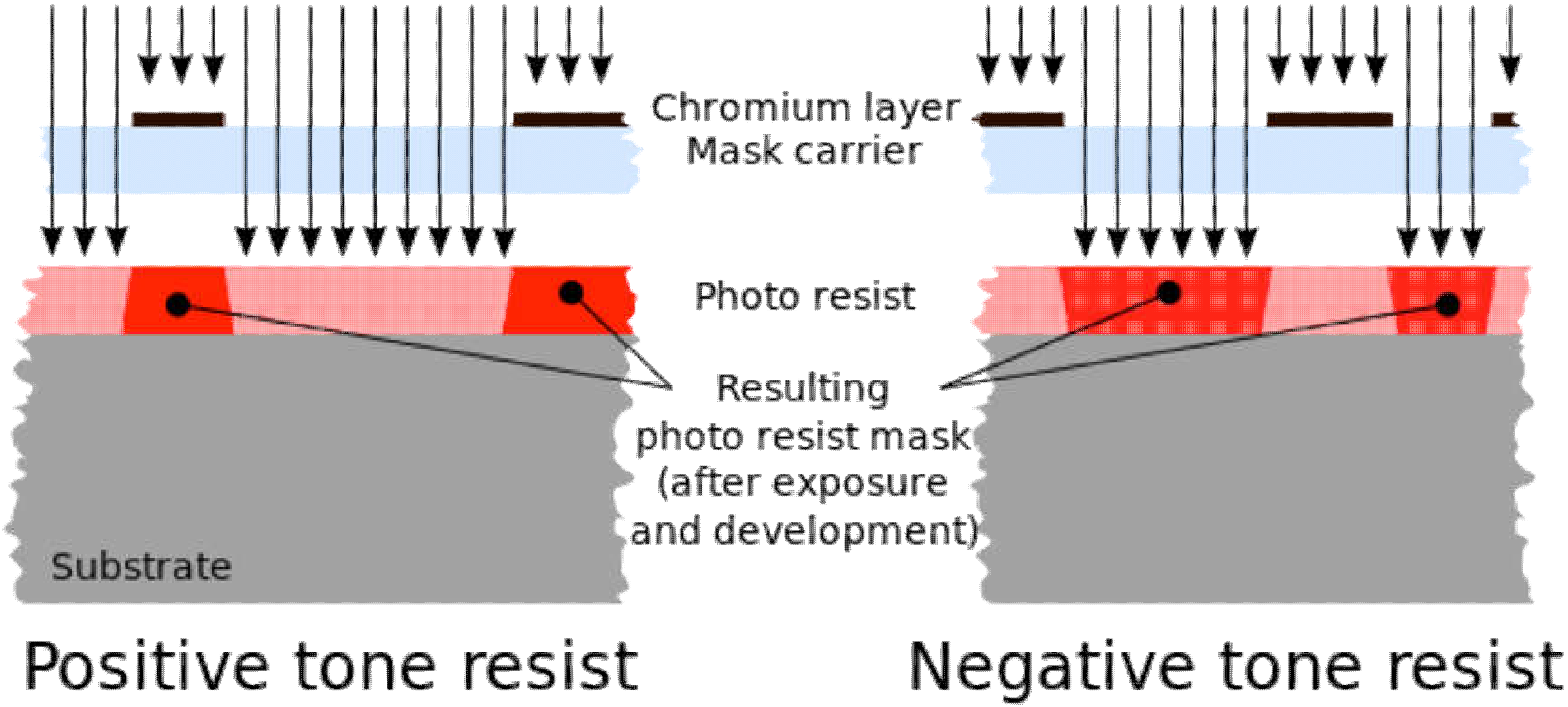
Dry Resist

- **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

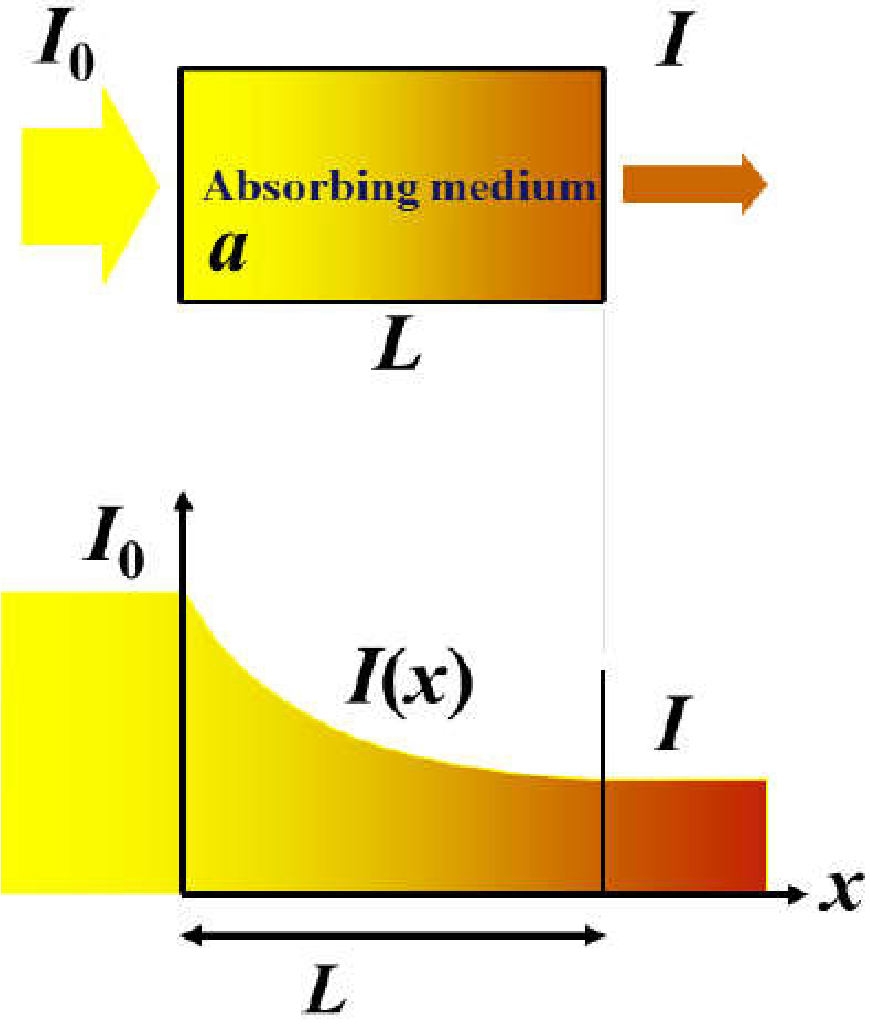
Lambert Beer's law

$$\boxed{I = I_0 \exp(-\alpha L)}$$

thicker films require larger exposure dose

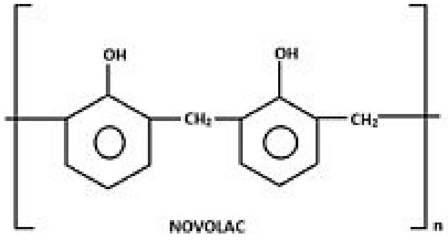
THICKNESS microns	EXPOSURE ENERGY mJ/cm^2
0.5 - 2	60 - 80
3 - 5	90 - 105
6 - 15	110 - 140
16 - 25	140 - 150
26 - 40	150 - 160

example: SU-8 resist

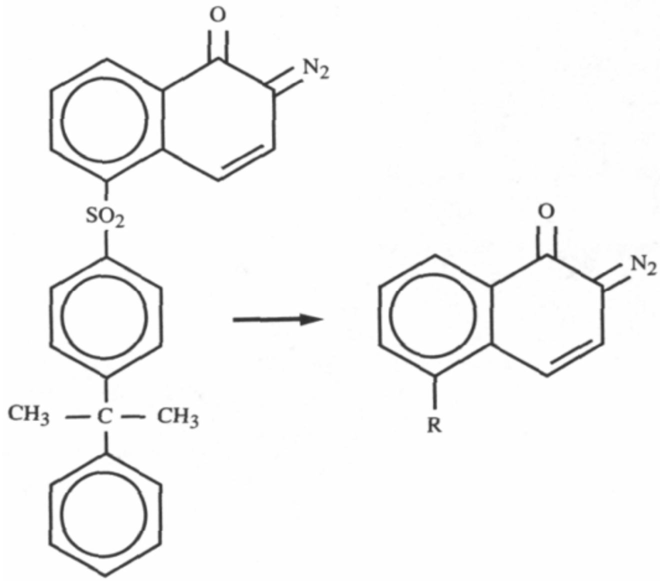


Positive Resist: Example

- **Base resin**
  - novolac
- **Photoactive compound (PAC)**
  - diazoquinone (DQ)
  - photosensitive
- **Solvent**
  - n-butyl acetate, xylene, ...
  - volatile
  - control viscosity, film thickness, ...

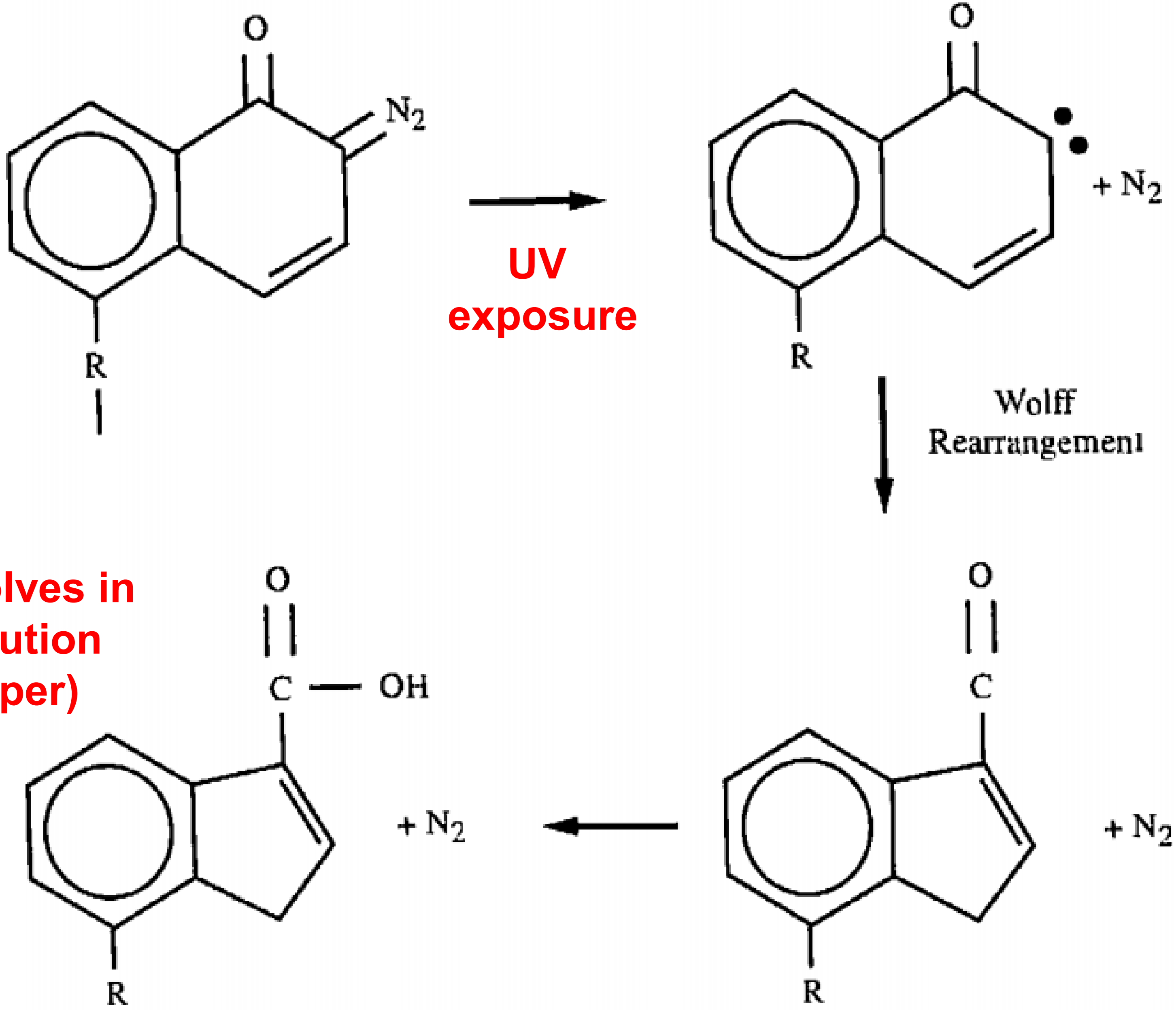


novolac



DQ

Positive Resist: Example



DQ

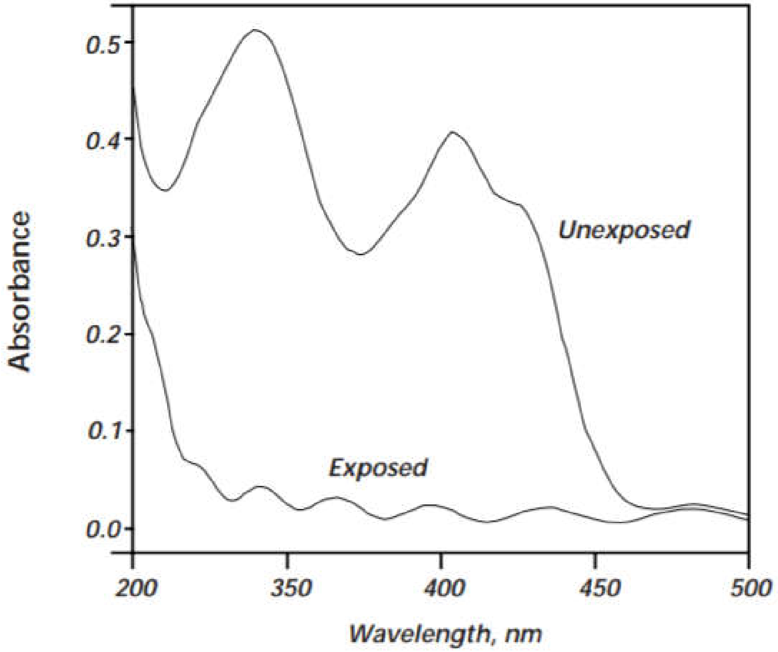
UV exposure

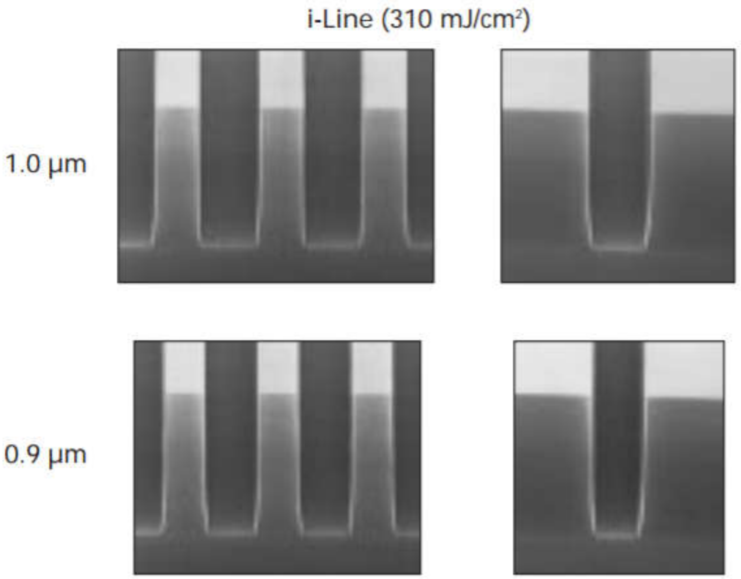
acid dissolves in base solution (developer)

Positive Resist: Example

Process for SPR220-v3.0

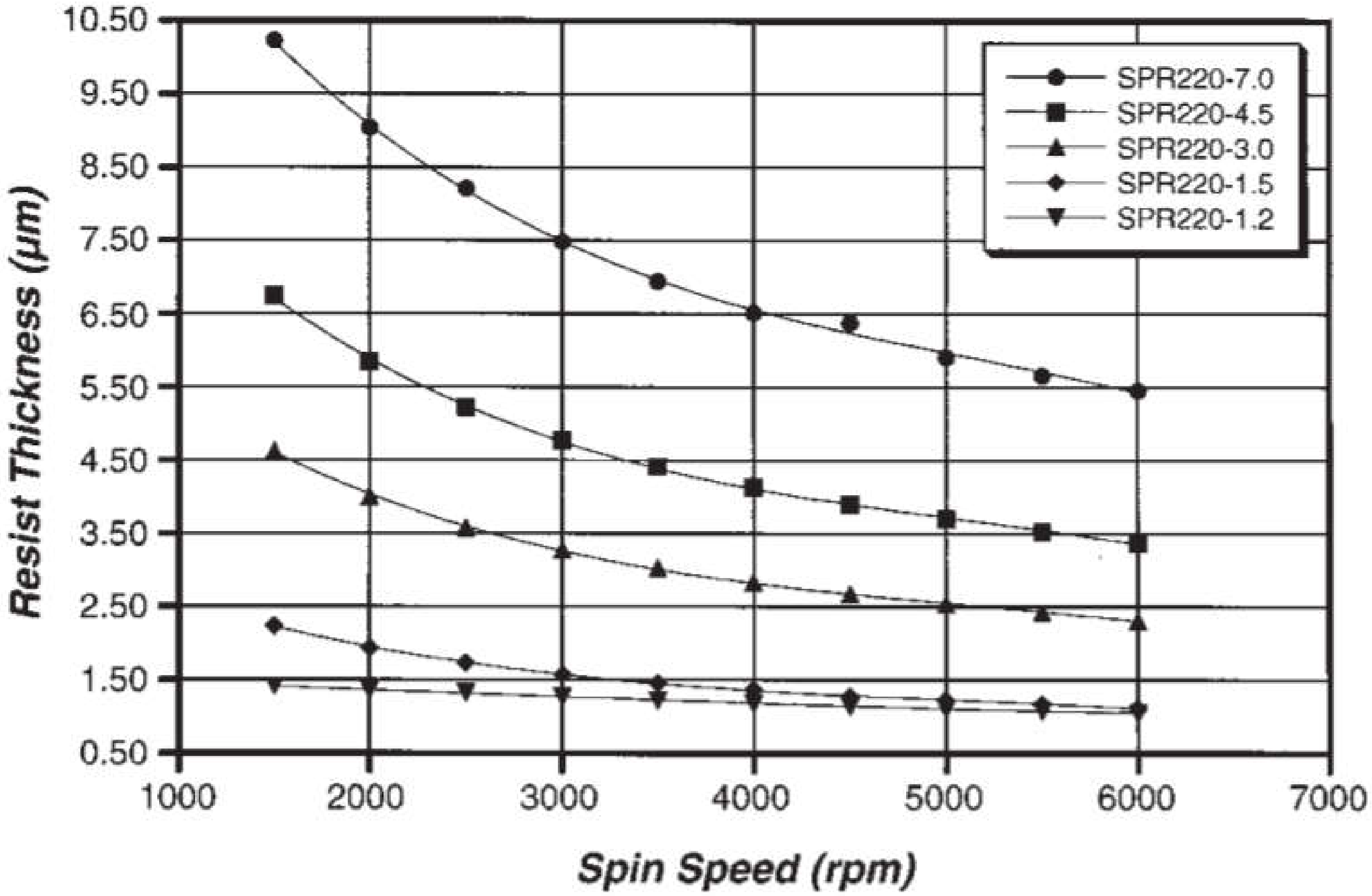
- clean sample (glass or silicon)
  - acetone / isopropanol / DI water, N_2 gas blow
- dehydration bake at 110 C, 10 mins
  - remove moisture
- spin coat SPR220-v3.0, 3000 rpm, 40 sec
- soft bake at 110 C, 90 sec
  - evaporate solvent
- UV expose (i-line), 300 mJ/cm^2
- post-exposure bake at 110 C, 90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





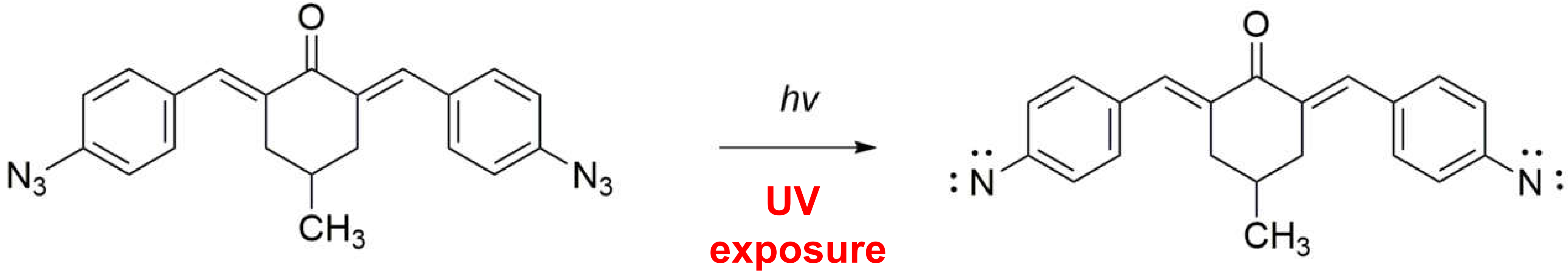
Positive Resist: Example

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



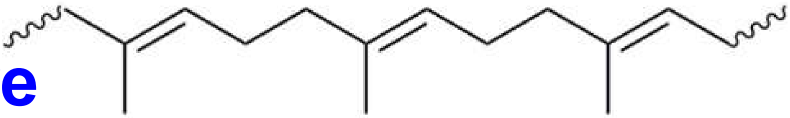
Negative Resist: Example

soluble in organic developer



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

heating



polyisoprene

Crosslinked insoluable polymer

Negative resists are long-chain polymers

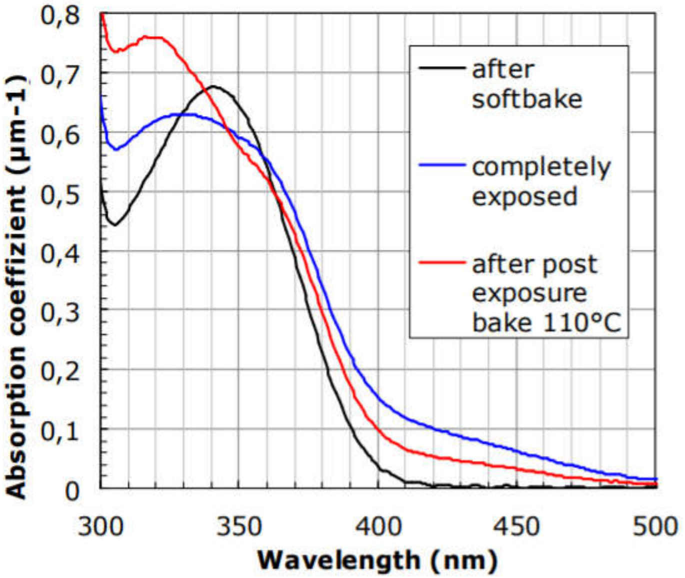
only used for features > 2 μm

insoluble in organic developer

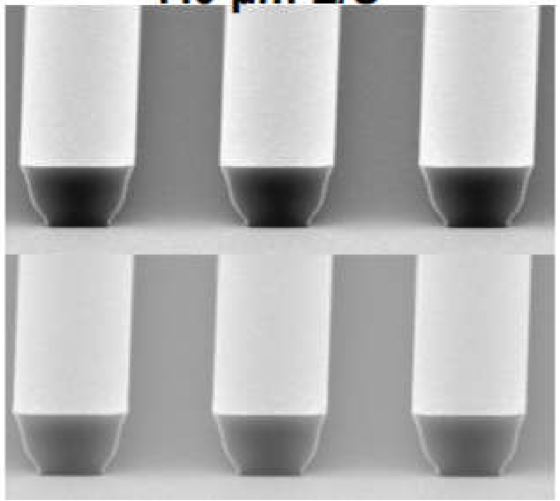
Negative Resist: Example

Process for AZ nLoF 2070

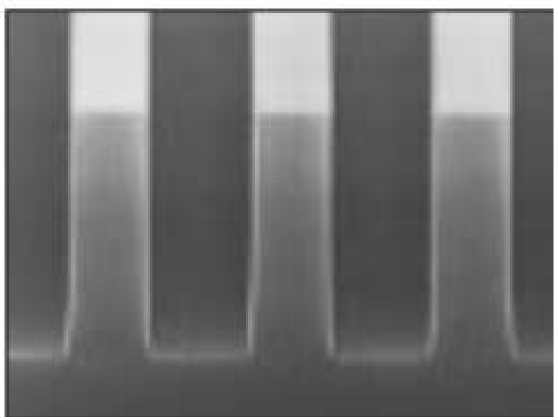
- clean sample (glass or silicon)
  - acetone / isopropanol / DI water, N_2 gas blow
- dehydration bake at 110 C, 10 mins
  - remove moisture
- spin coat AZ nLoF 2070, 3000 rpm, 40 sec
- soft bake at 110 C, 90 sec
  - evaporate solvent
- UV expose (i-line), 50 mJ/cm^2
- post-exposure bake at 110 C, 90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

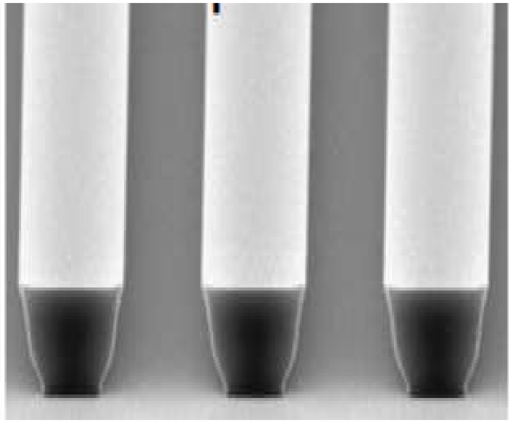


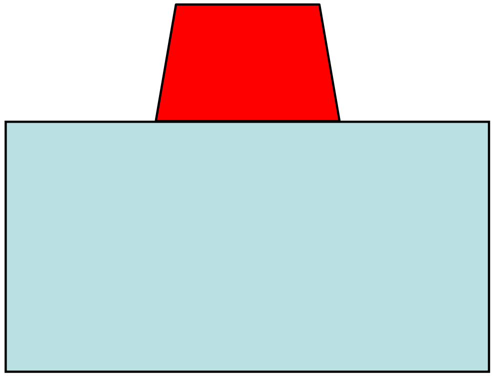
7.0 µm L/S

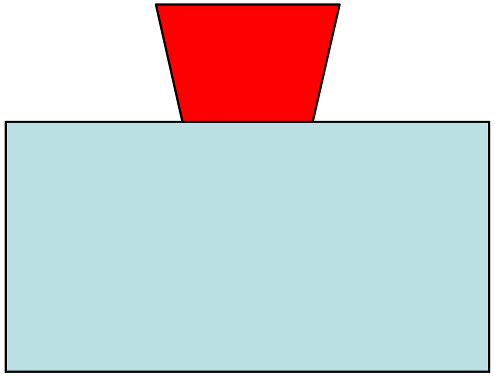


Positive vs. Negative



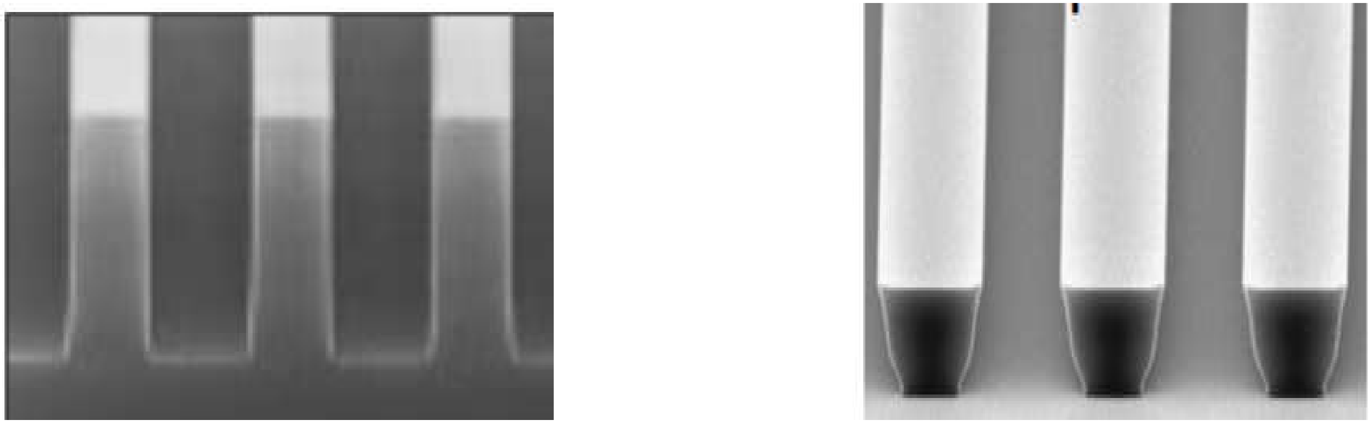


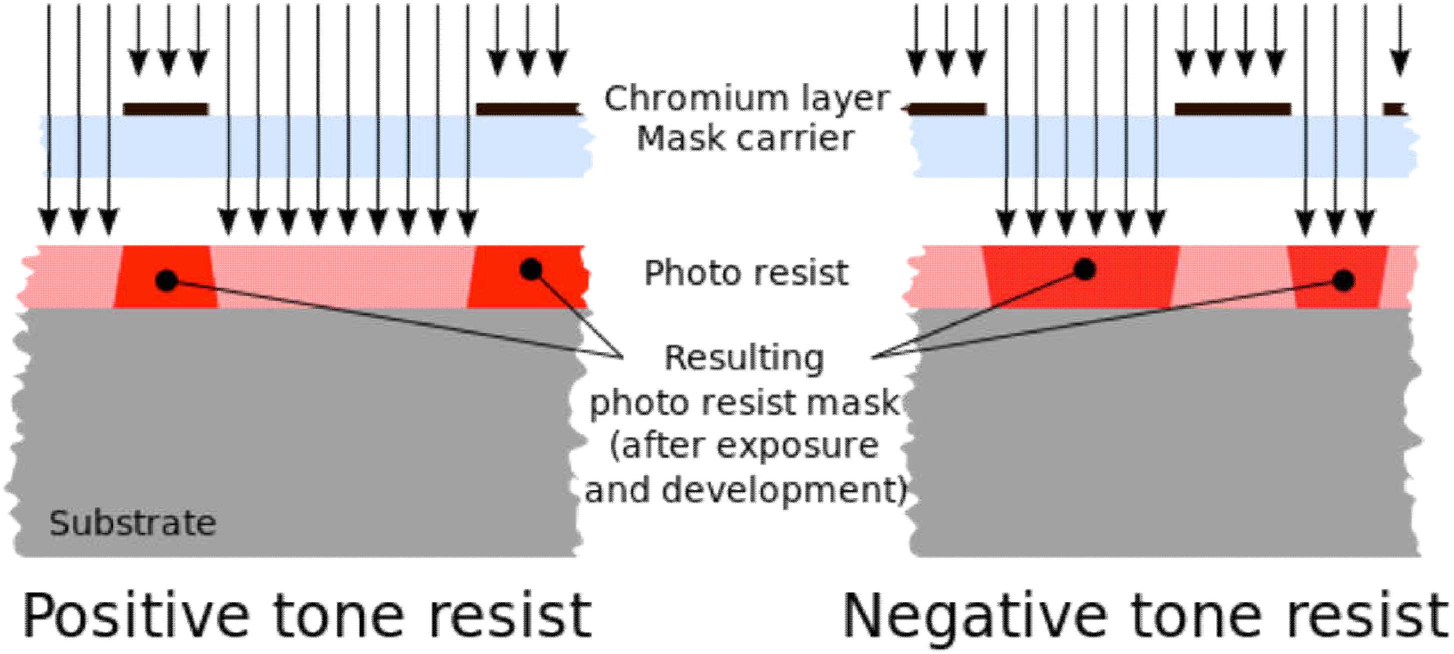




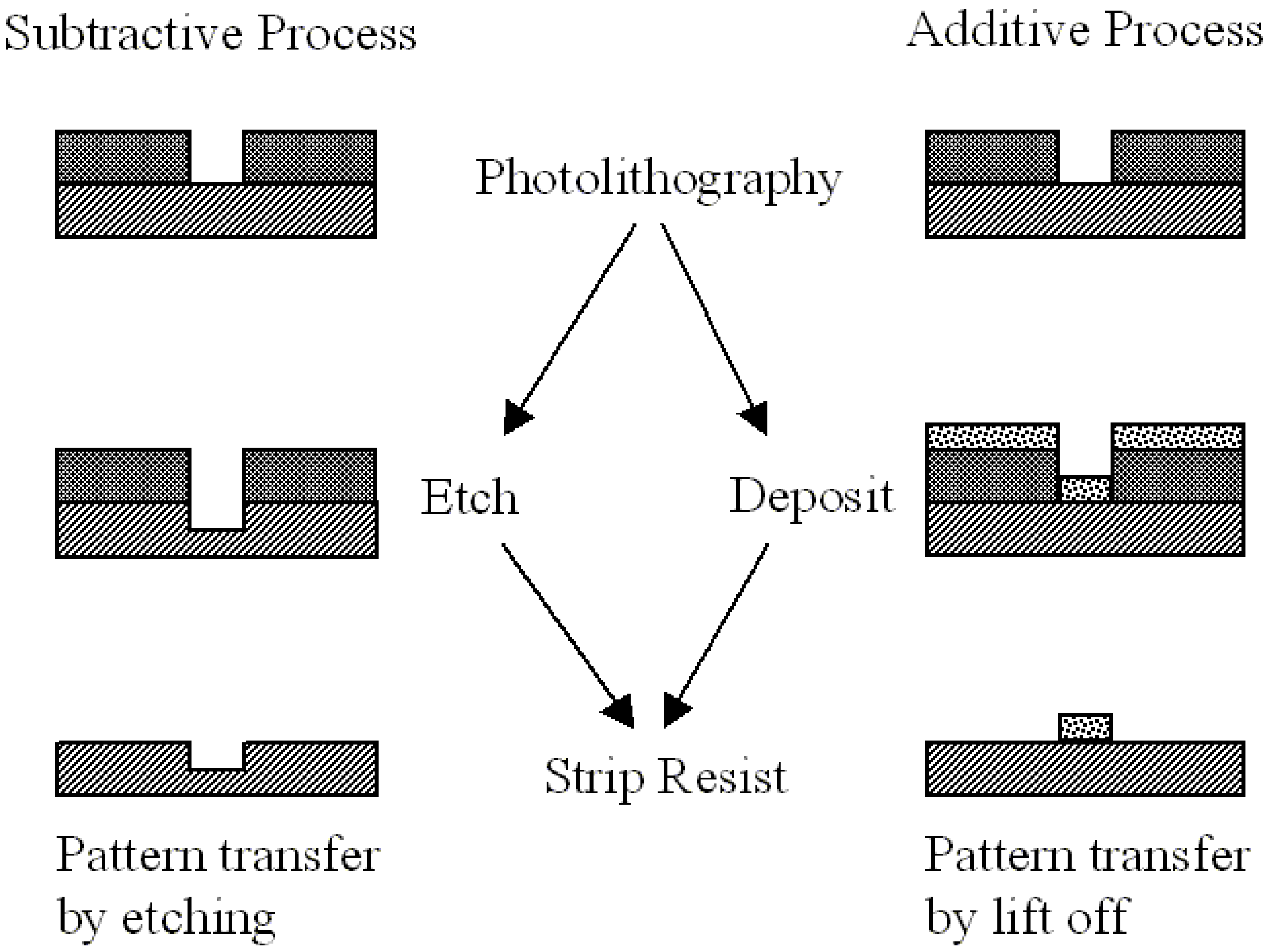
?

Positive vs. Negative





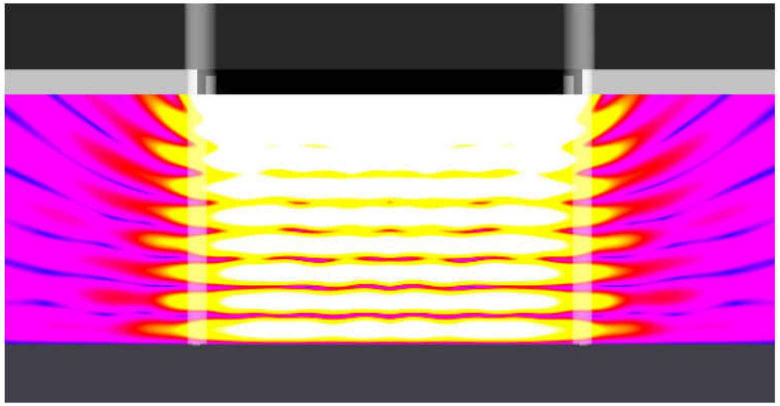
Pattern Transfer

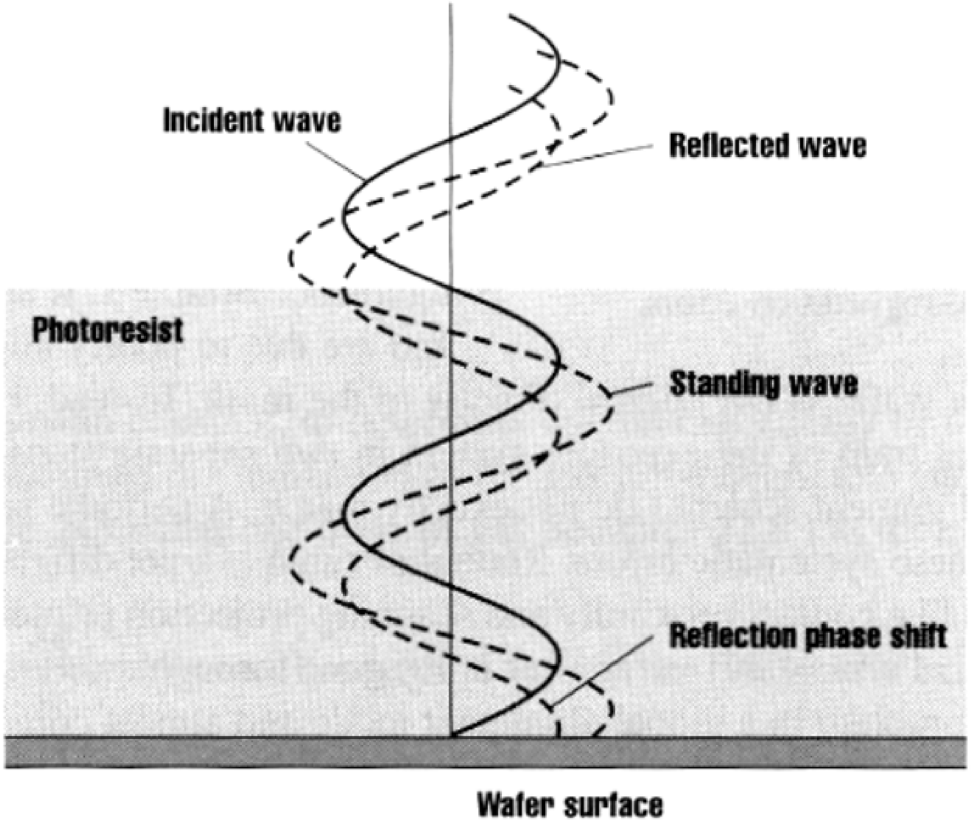


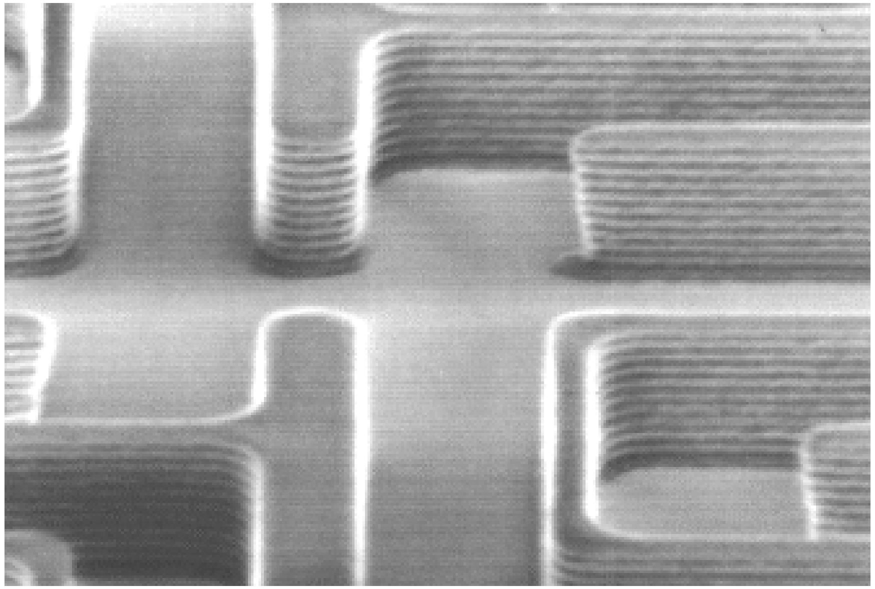
positive resist - etching

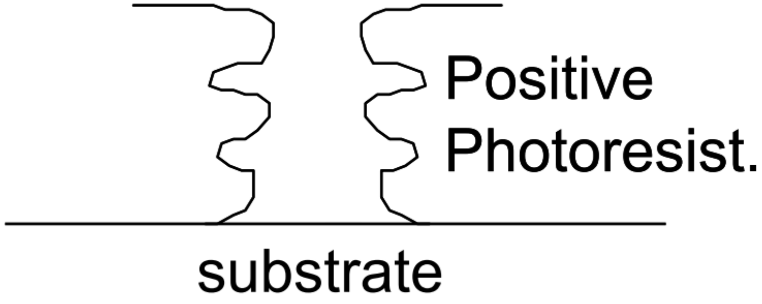
negative resist - liftoff

Standing Waves

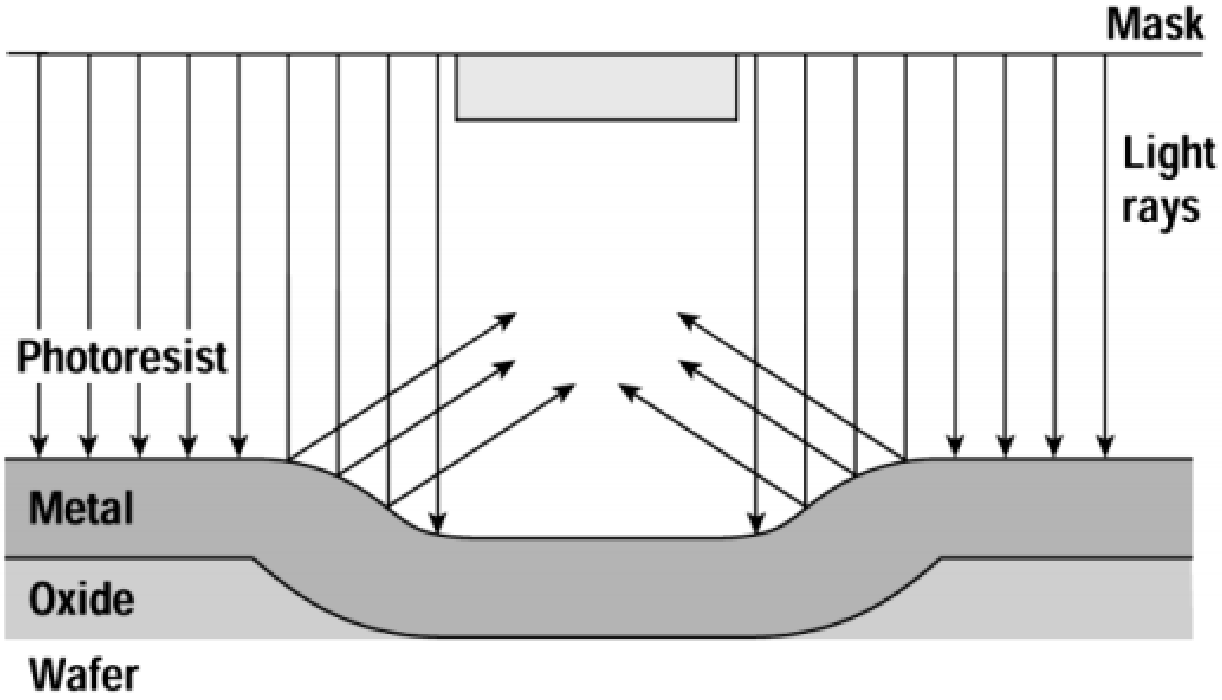


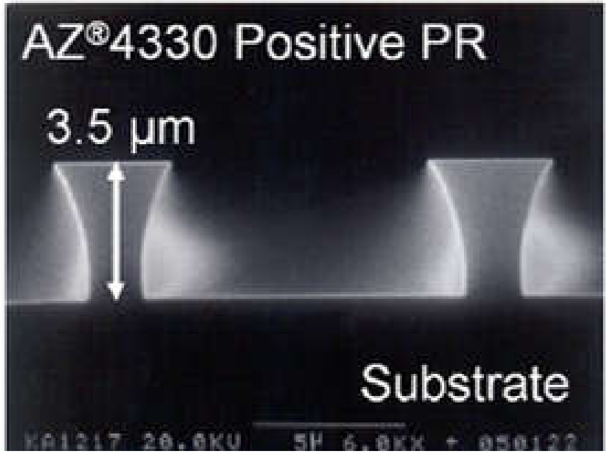


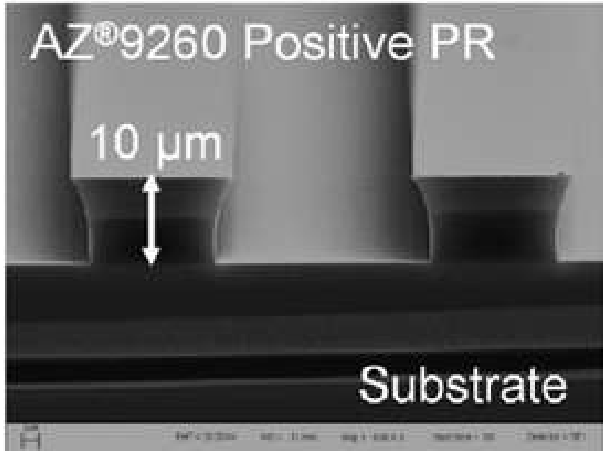




Proximity Scattering

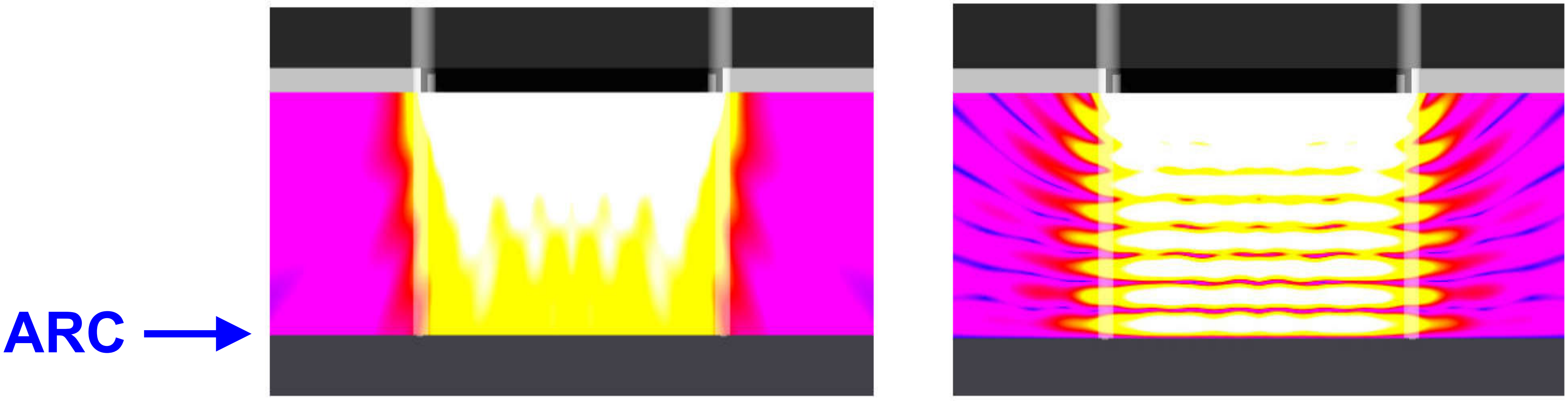






Reducing Substrate Effects

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

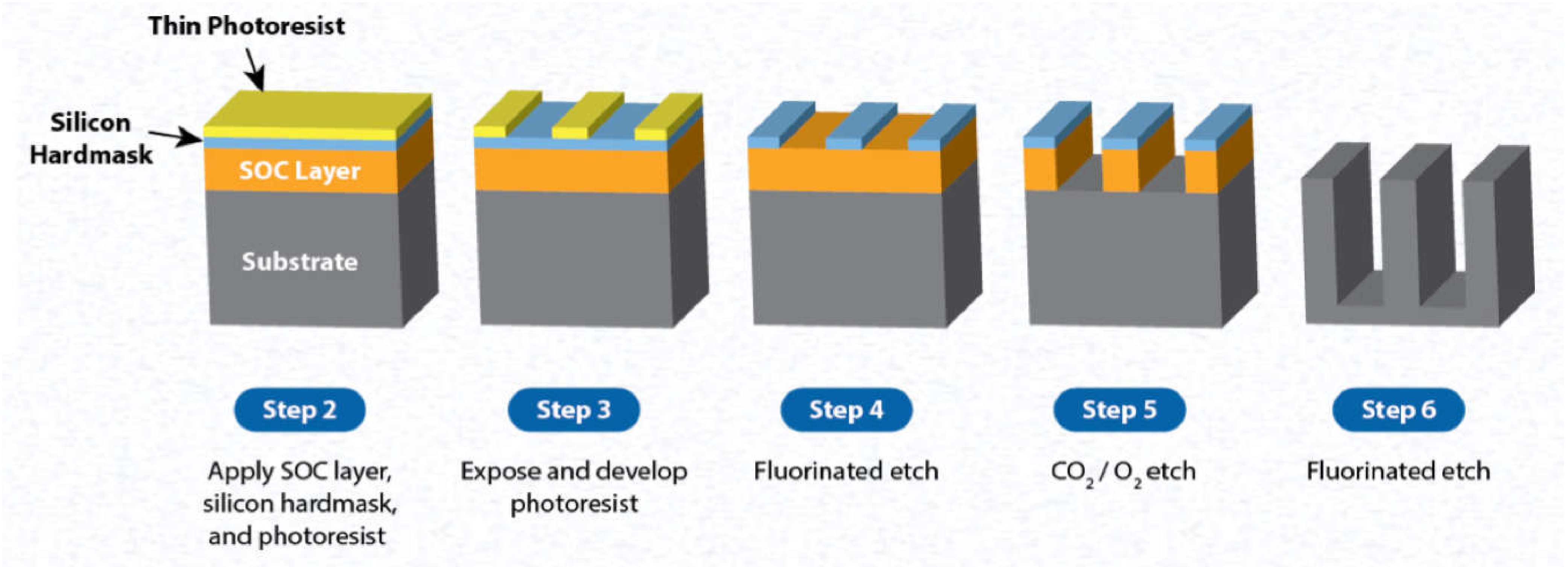


with ARC

without ARC

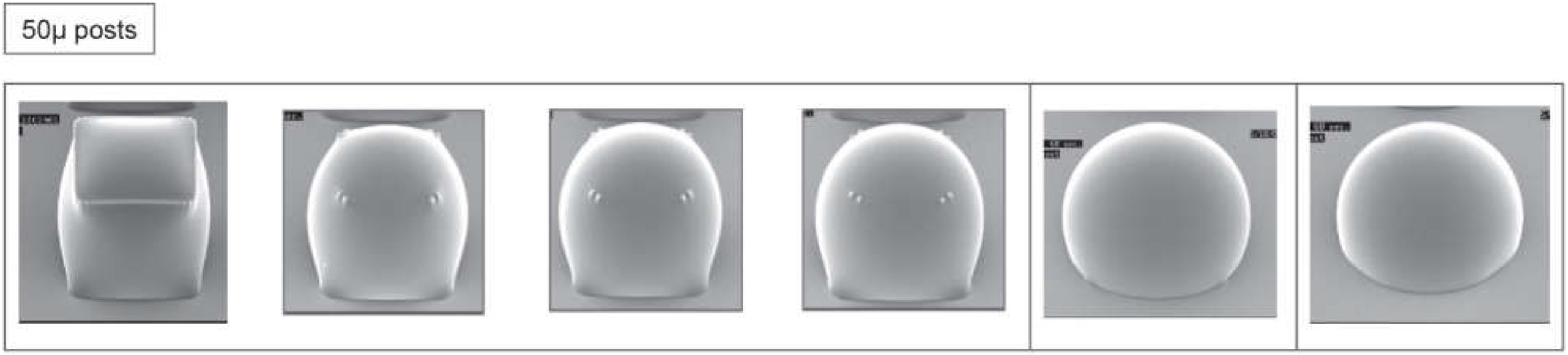
Reducing Substrate Effects

- **Apply multilayer resists**

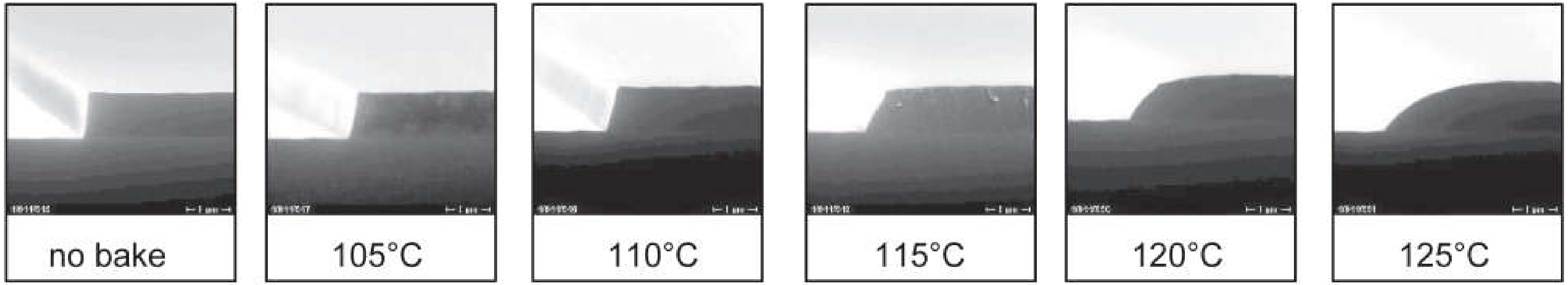


Photoresist Reflow

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



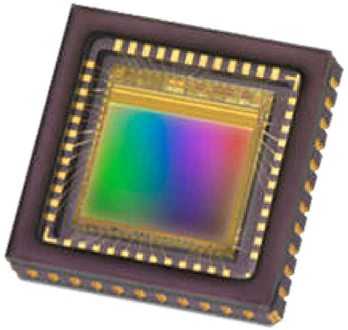
Reflow of AZ® 40 XT cubes at different temperatures and for different time. Images taken from the *AZ 40XT-11D Thermal Flow* data sheet of AZ-EM.

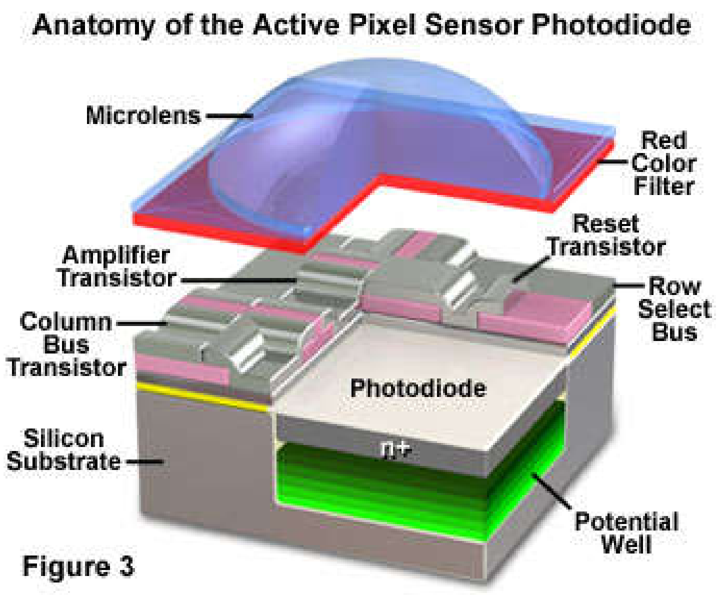


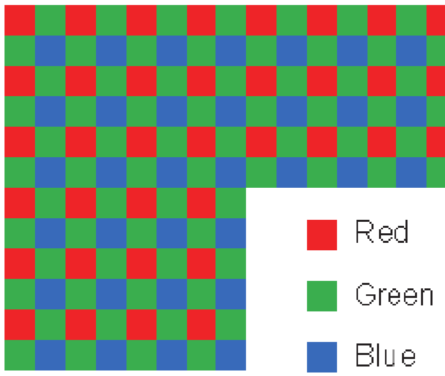
Photoresist Reflow

- **Microlens array by reflow**

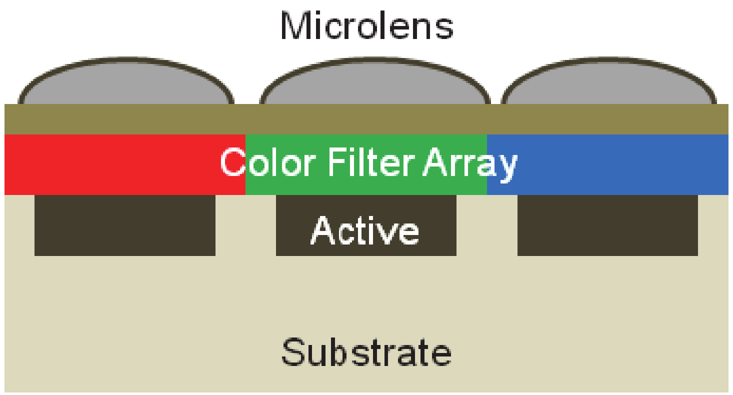
CMOS image sensor







Bayer Filter Pattern



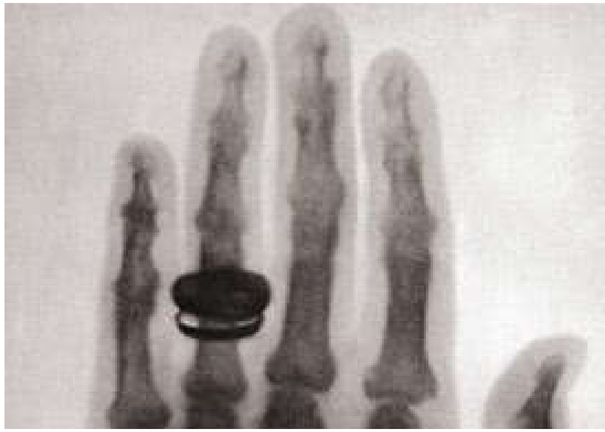
Imager Photodiode cross-section

Photoresist Removal

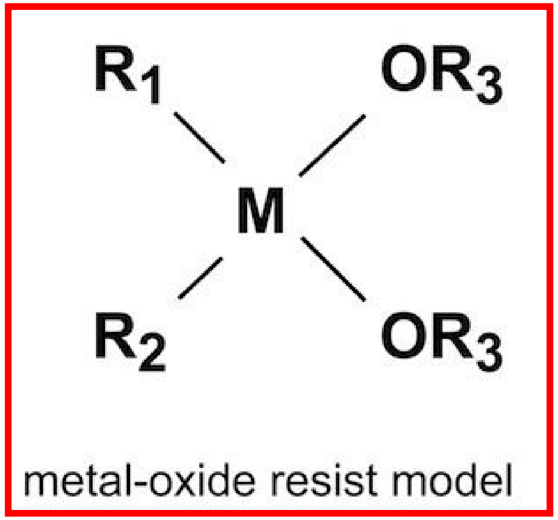
- Organic solvents
  - acetone / isopropanol / DI water
  - NMP, DMSO, ...
- Highly cross-linked resist cannot be removed by solvents
- Oxygen plasma
  - polymer (C, H, O, ...) + O_2 = CO_2 + H_2O + ...

Resists for EUV Lithography

- EUV: 13.5 nm
- Common organic resists are transparent in EUV
- Use metal oxide based resists to absorb EUV



X-ray image



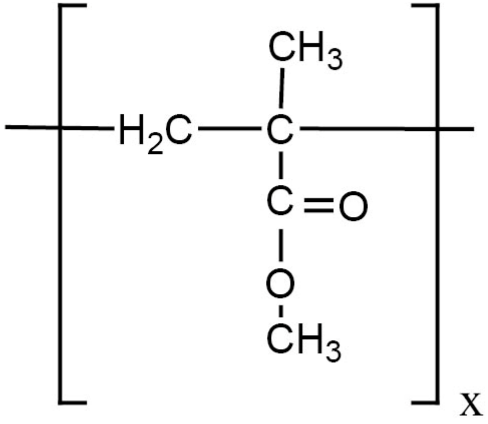
DOI: 10.1117/2.1201606.006534

Resists for E-Beam Lithography

- E-beam breaks or creates chemical bonds

- Positive resists
  - Chemical bonds break
  - e.g.: PMMA, PMMA/CoMAA, PMGI, ZEP520, ...

- Negative resists
  - Chemical bonds creation
  - e.g.: ma-N 2400, PMMA, calixarene, ...



PMMA: Poly(methyl methacrylate)

References for Photoresists

- **Useful notes for photolithography**

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

https://cleanroom.byu.edu/processes#Microfab_PhotoLith

- **Always read manuals before experiments**

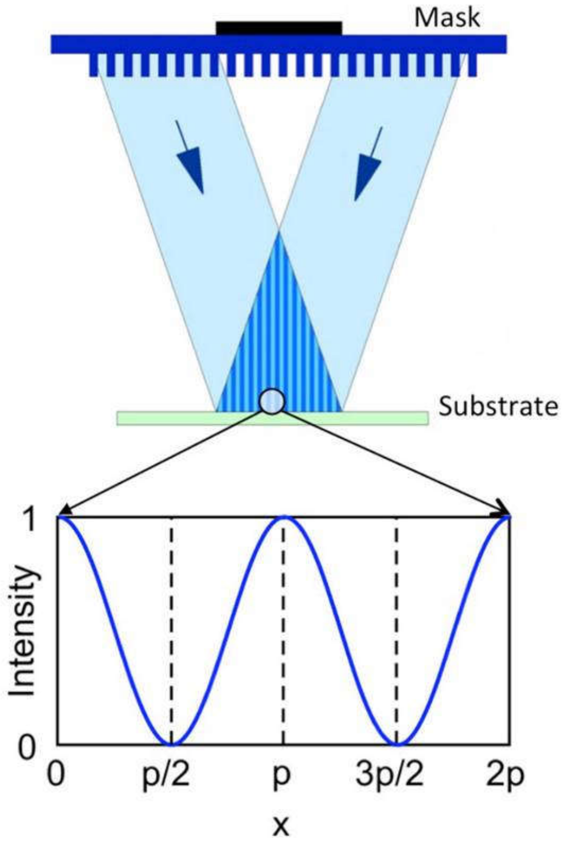
http://www.microchemicals.com/products/photoresists.html

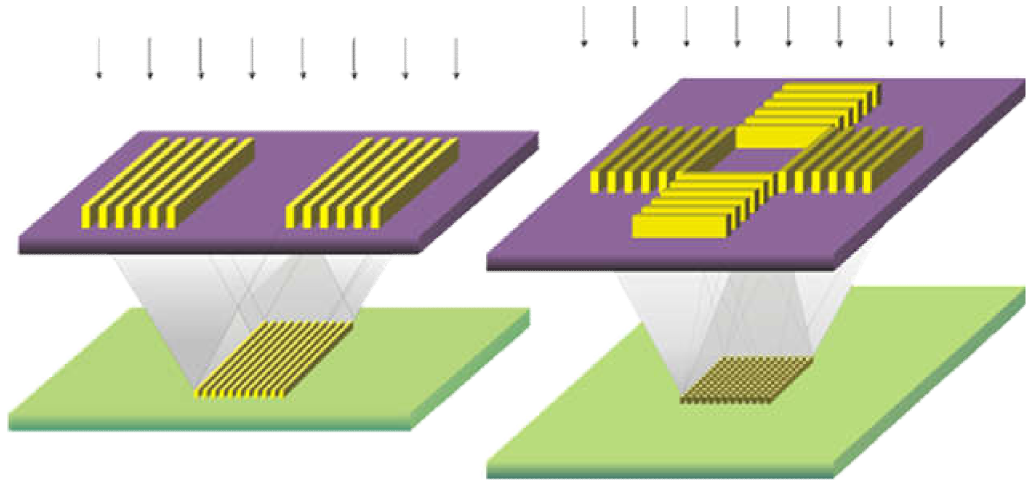
Advanced Lithography

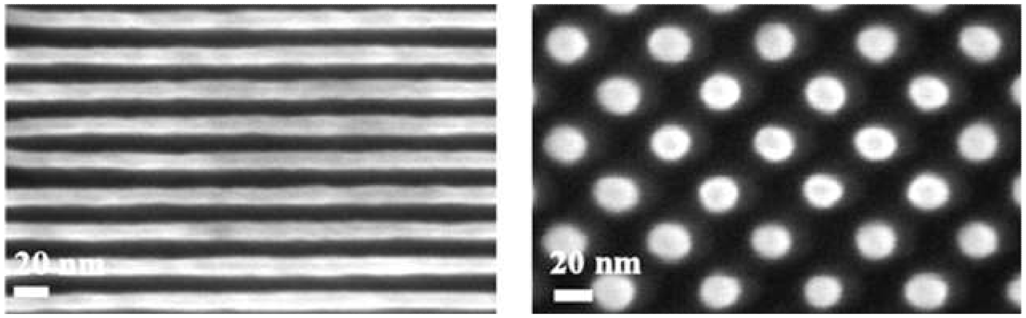
- Interference / holographic lithography
- Greyscale lithography
- 3D lithography
- Plasmonic lithography
- Nanoimprint lithography
- Directed self-assembly lithography
- Inorganic materials based lithography

Interference / Holographic Lithography

- **resolution ~ $\lambda/2$**
    - easy to form periodic patterns

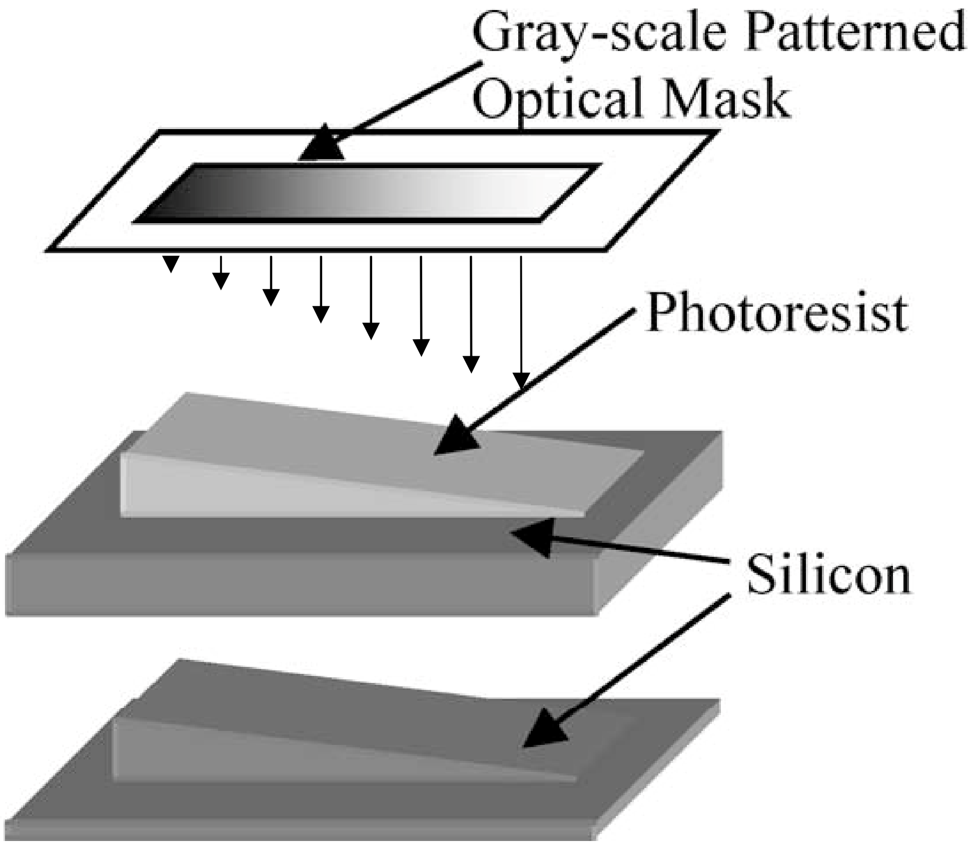


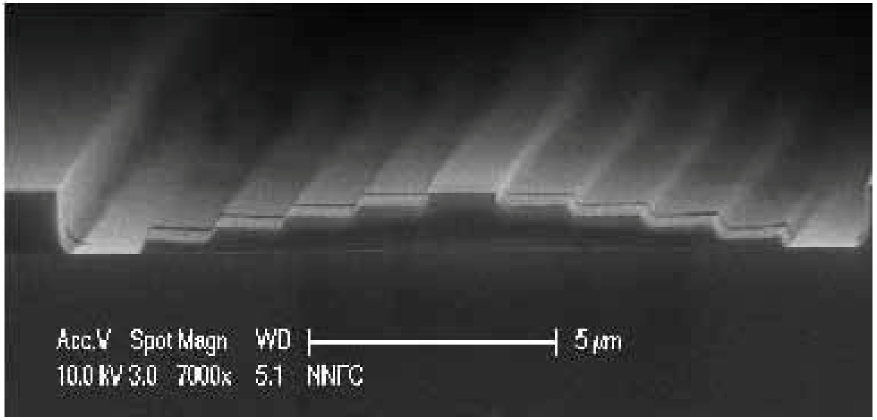


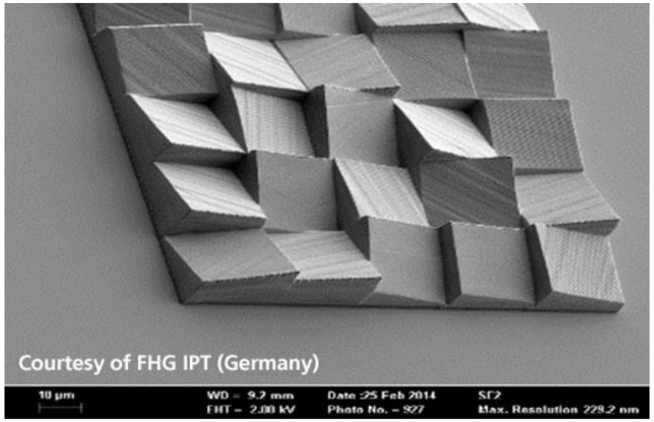


Greyscale Lithography

- **resist development ~ exposure dose**

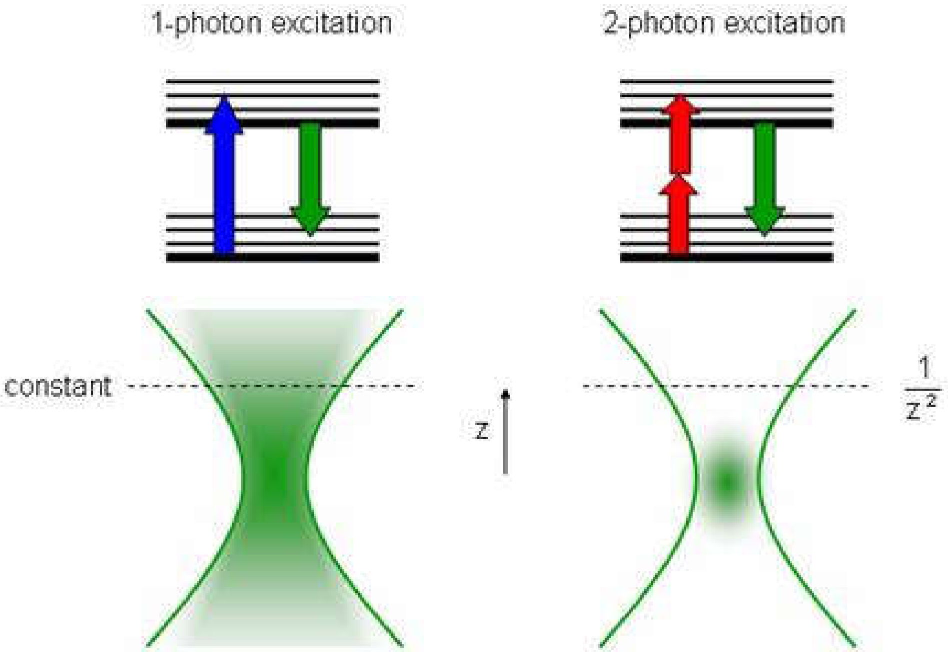




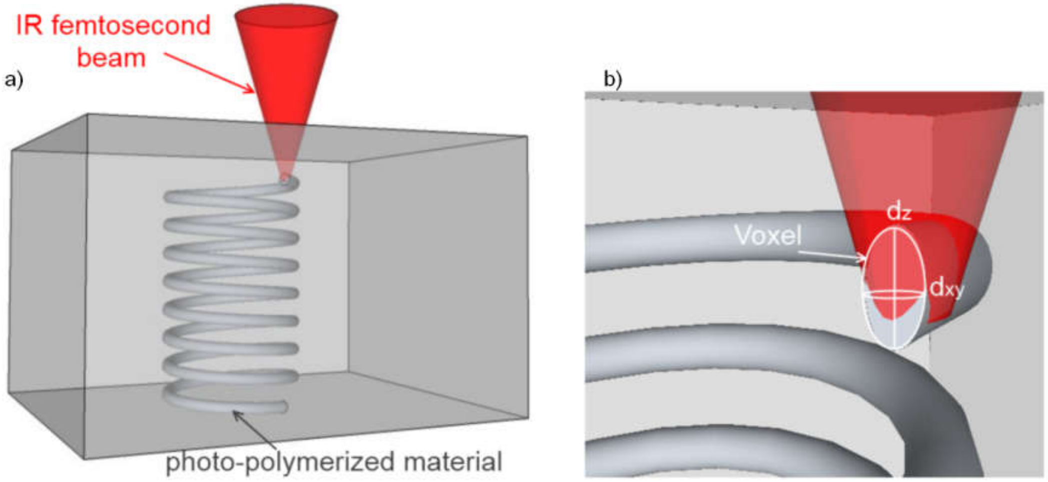

Courtesy of FHG IPT (Germany)

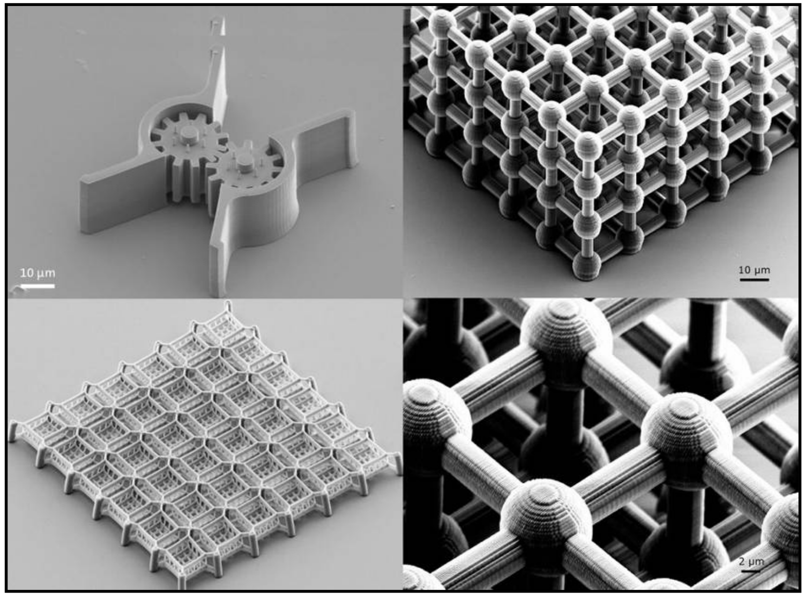
Multi-Photon Lithography

- **direct laser writing**
  - **multi-photon absorption**

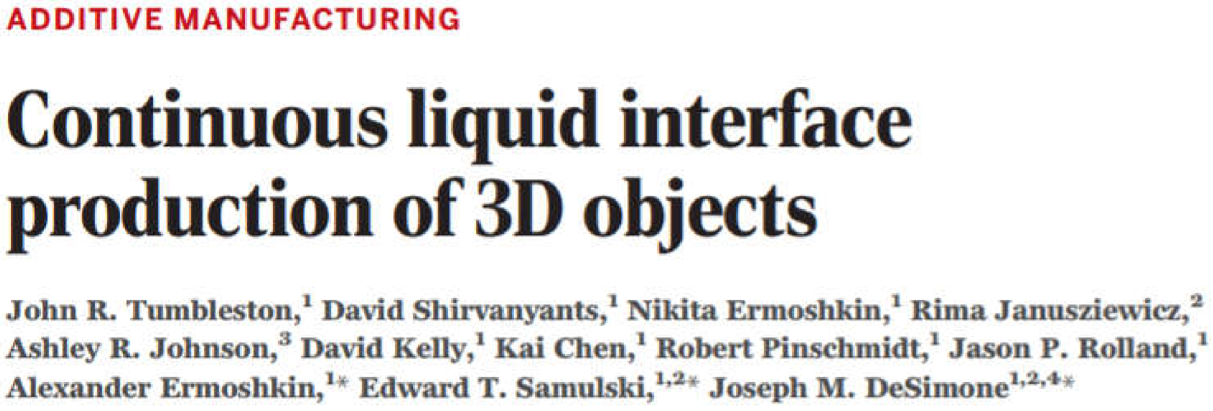


nonlinear optical effect





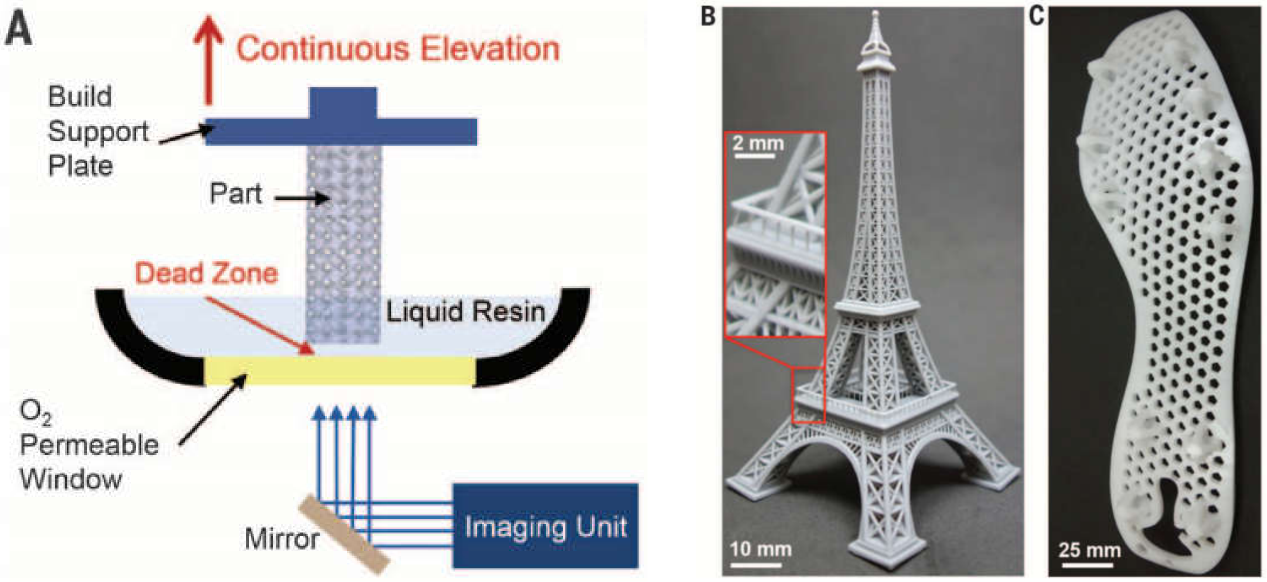
3D Lithography



ADDITIVE MANUFACTURING

Continuous liquid interface production of 3D objects

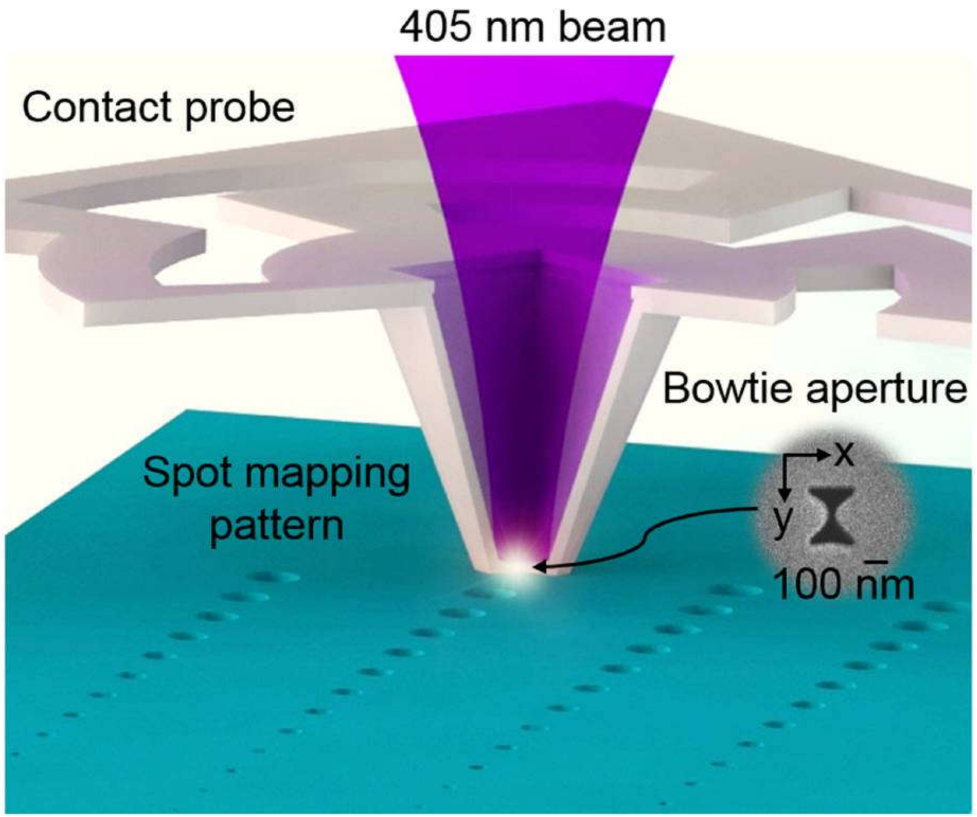
John R. Tumbleston,[1] David Shirvanyants,[1] Nikita Ermoshkin,[1] Rima Janusziewicz,[2] Ashley R. Johnson,[3] David Kelly,[1] Kai Chen,[1] Robert Pinschmidt,[1] Jason P. Rolland,[1] Alexander Ermoshkin,[1]* Edward T. Samulski,[1,2]* Joseph M. DeSimone[1,2,4]*



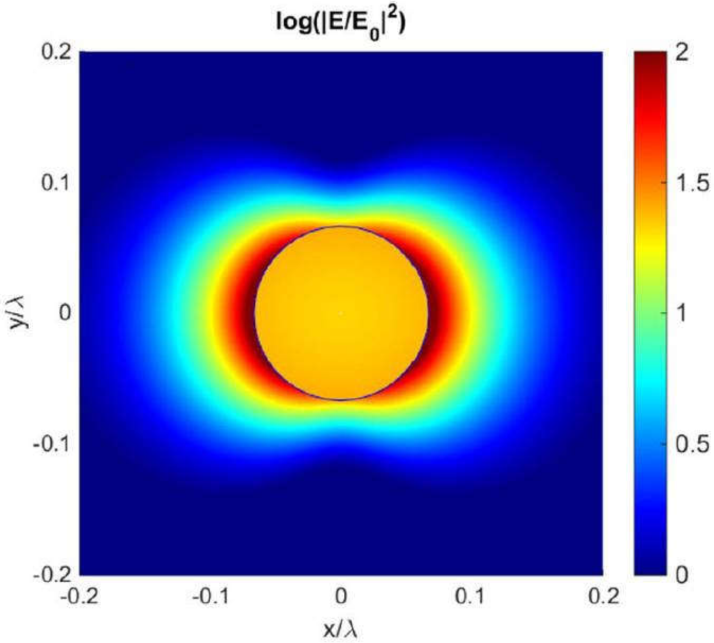
Video

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

Plasmonic Lithography



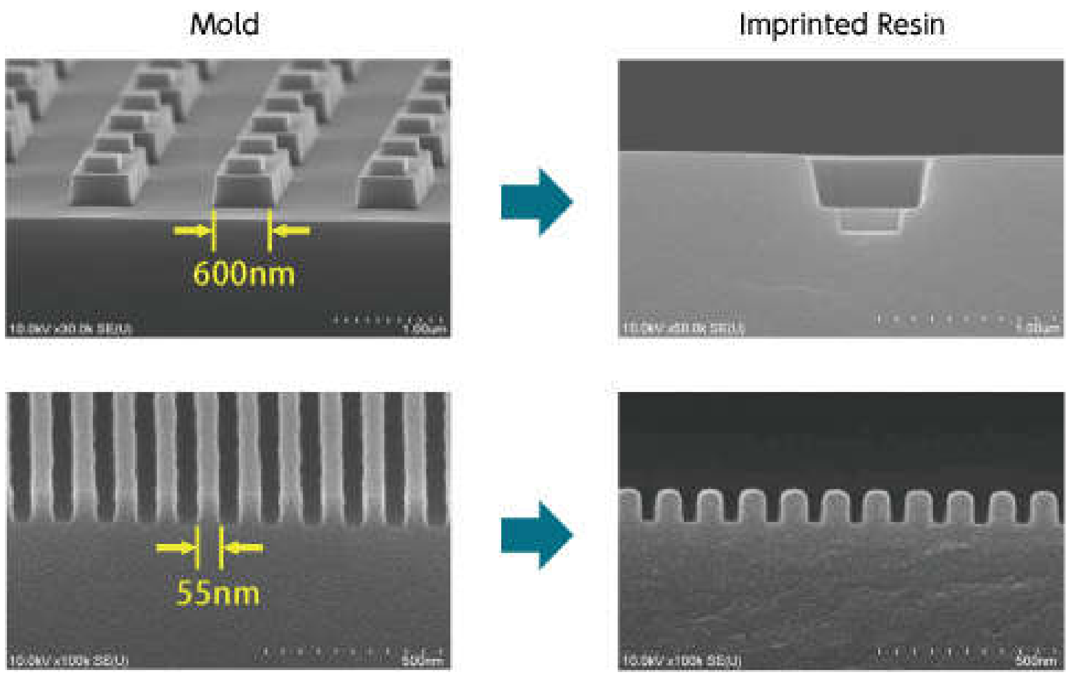
subwavelength resolution

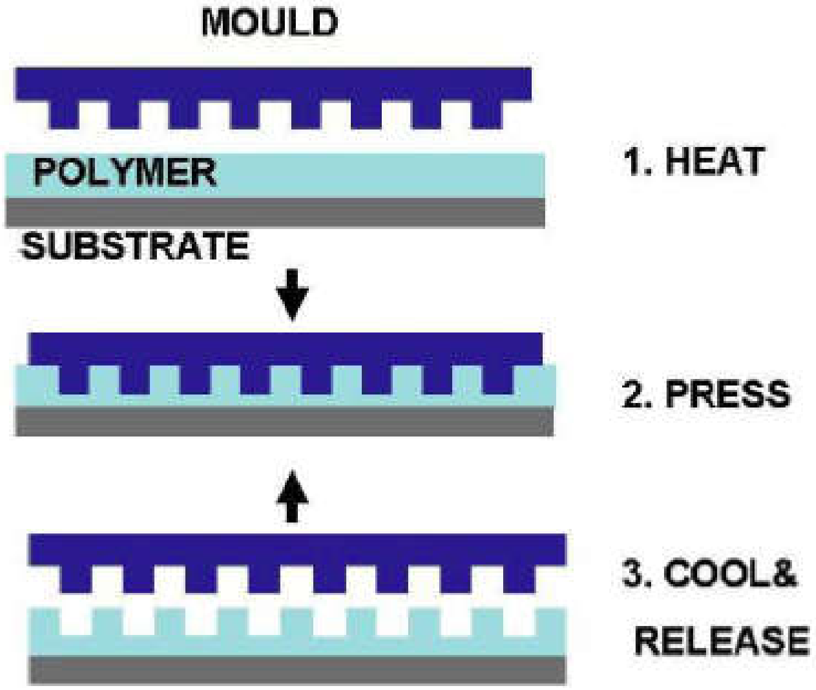


field enhancement at metal surfaces

Nanoimprint Lithography

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

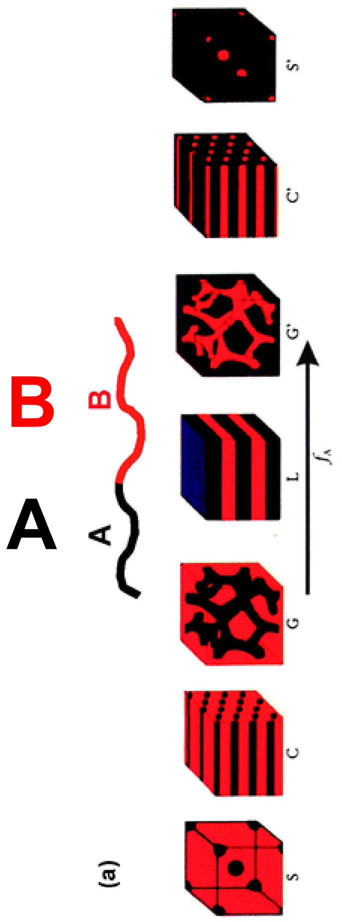


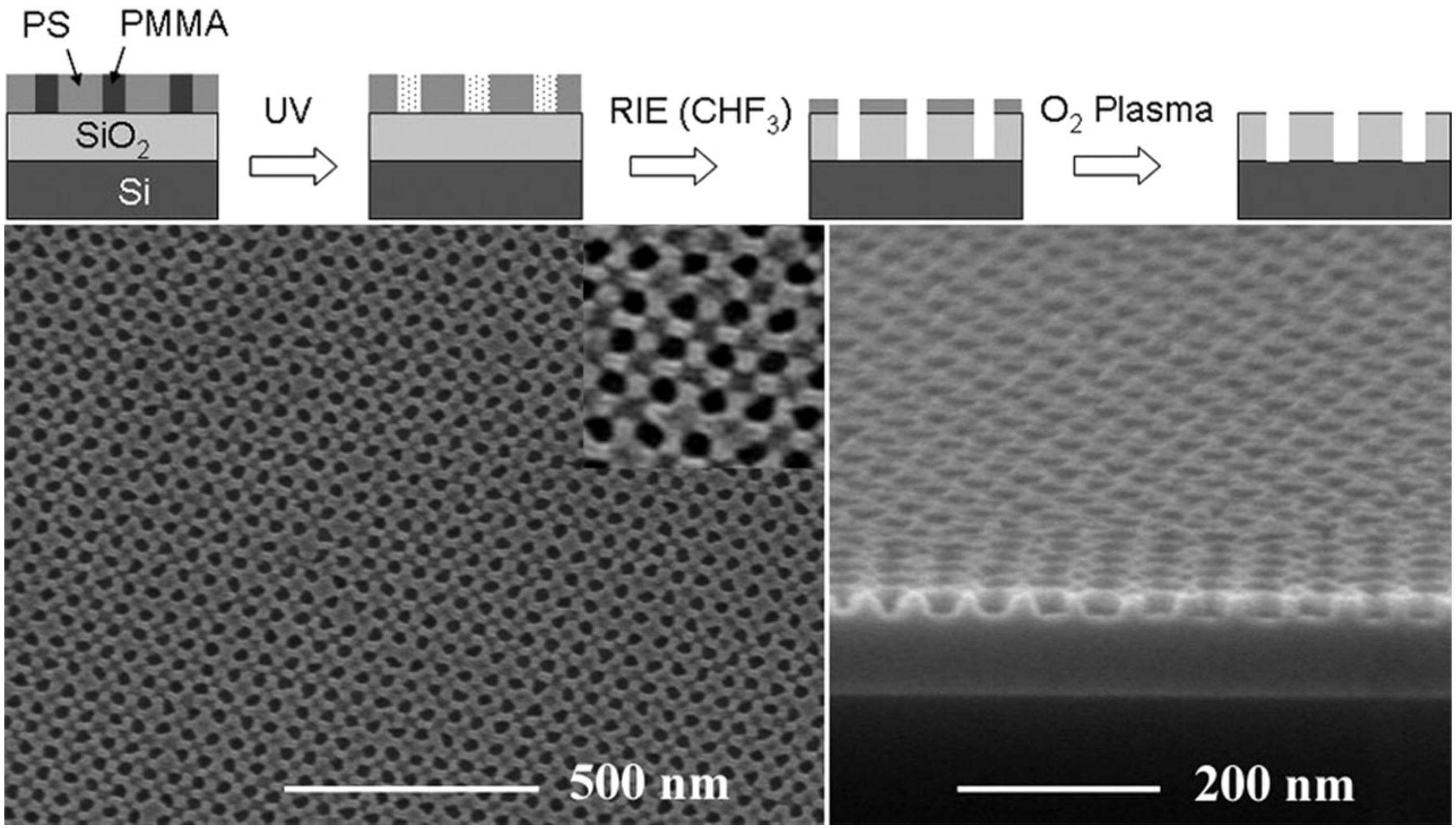


S. Y. Chou, et al., *Science* **272,** 5258 (1996)

Direct Self-assembly

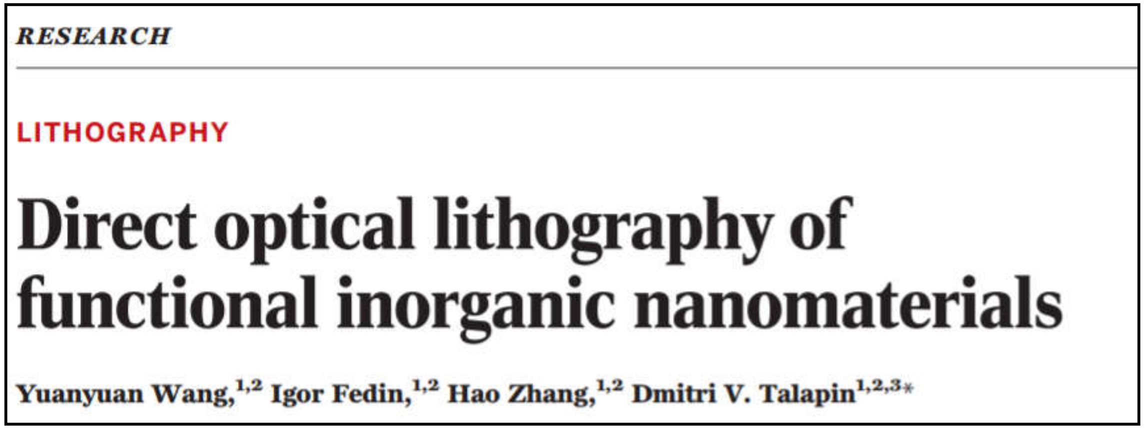
- **Phase separation by block copolymers**





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

Lithography of Inorganic Materials

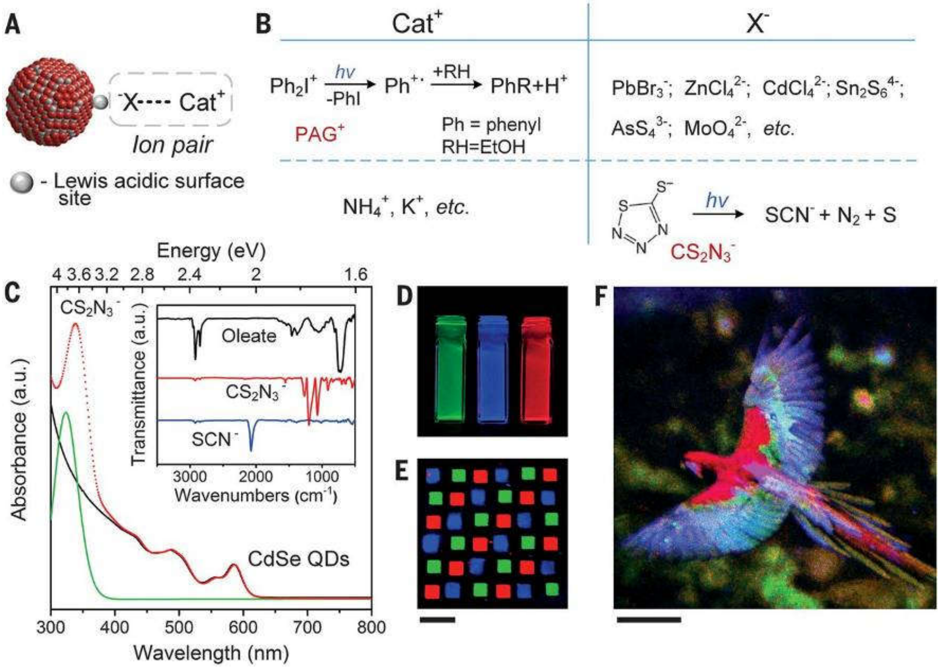


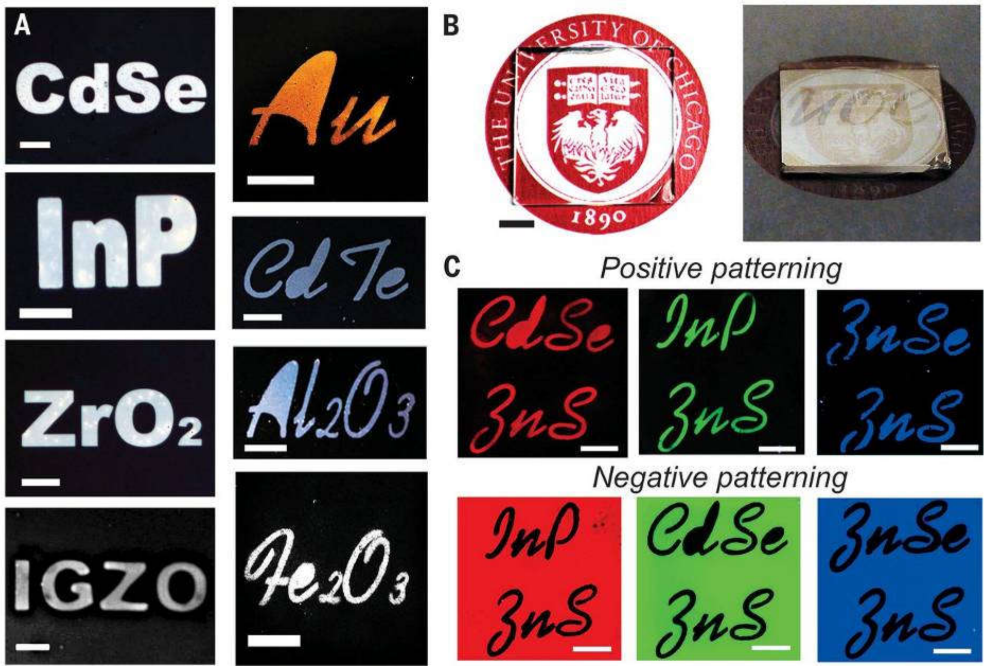
RESEARCH

LITHOGRAPHY

Direct optical lithography of functional inorganic nanomaterials

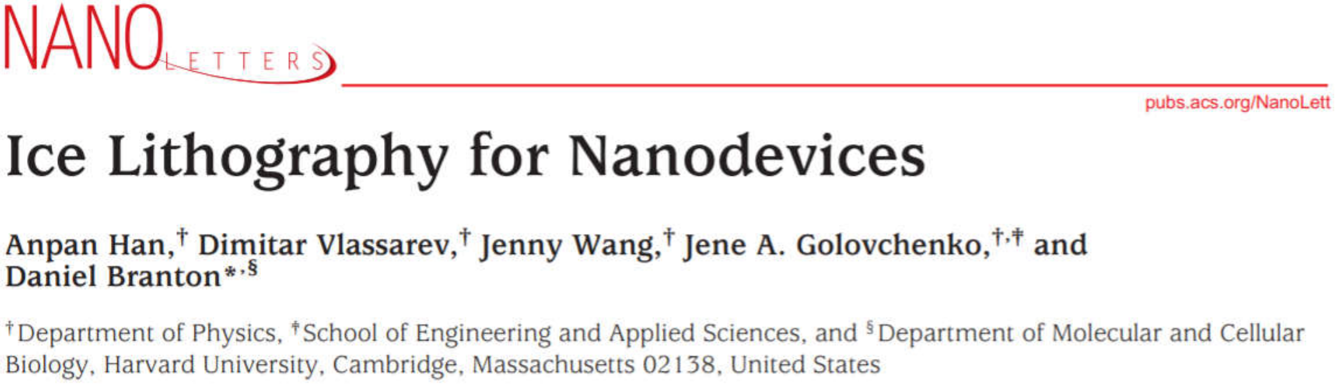
Yuanyuan Wang,[1,2] Igor Fedin,[1,2] Hao Zhang,[1,2] Dmitri V. Talapin[1,2,3]*





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

Ice Lithography



NANO LETTERS

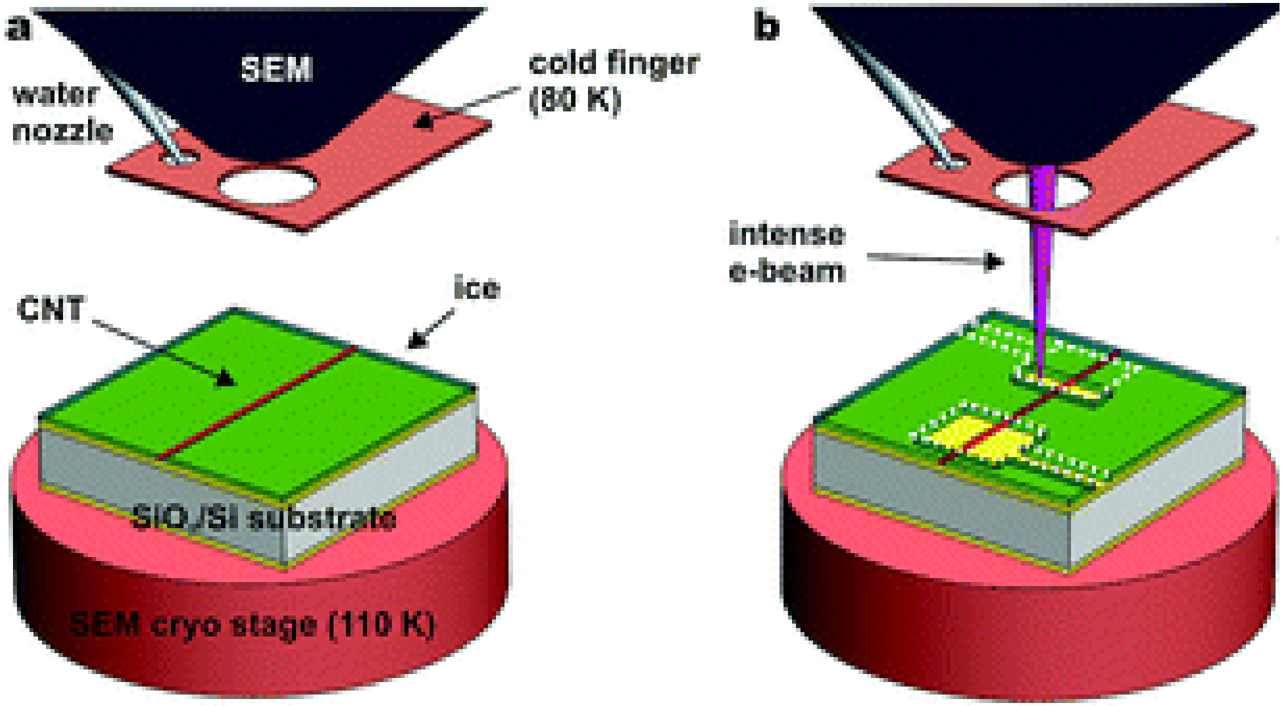
pubs.acs.org/NanoLett

Ice Lithography for Nanodevices

Anpan Han,[†] Dimitar Vlassarev,[†] Jenny Wang,[†] Jene A. Golovchenko,[†,‡] and Daniel Branton[*,§]

[†]Department of Physics, [‡]School of Engineering and Applied Sciences, and [§]Department of Molecular and Cellular Biology, Harvard University, Cambridge, Massachusetts 02138, United States

pattern in vacuum
no solvents



mapping CNT under ice

writing in ice

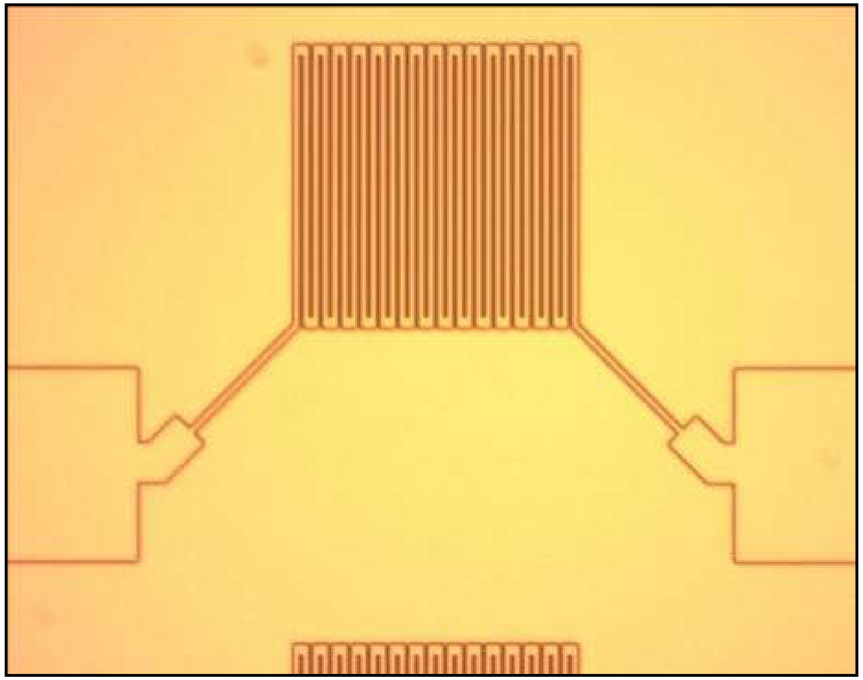
A. Han, et al., *Nano Lett.* **10,** 5056 (2010)

Metrology

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

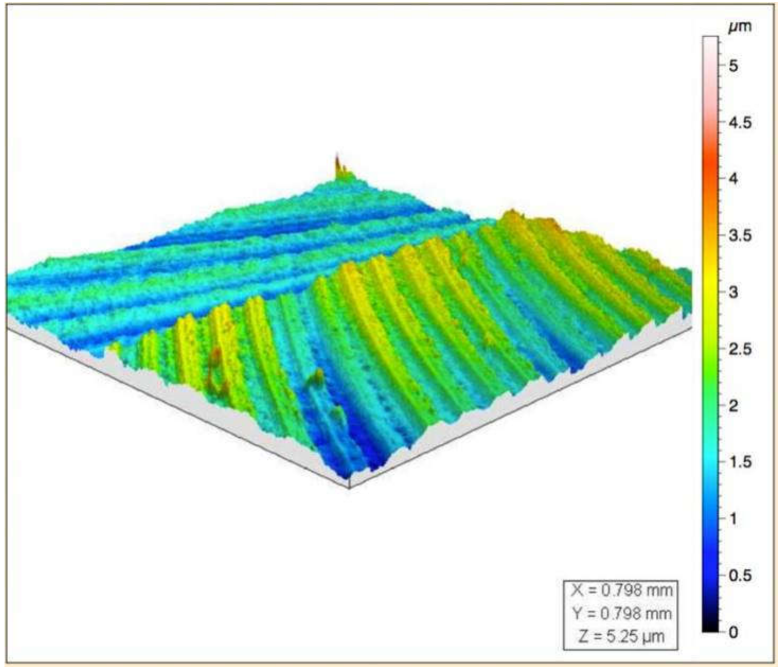
Metrology

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



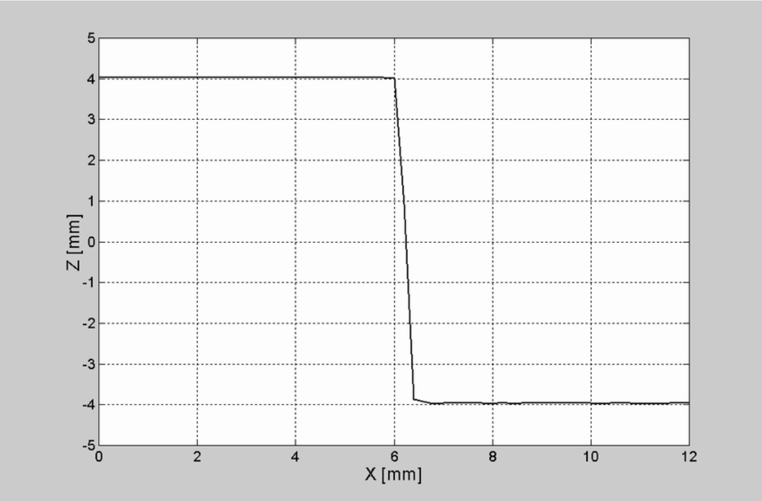
Metrology

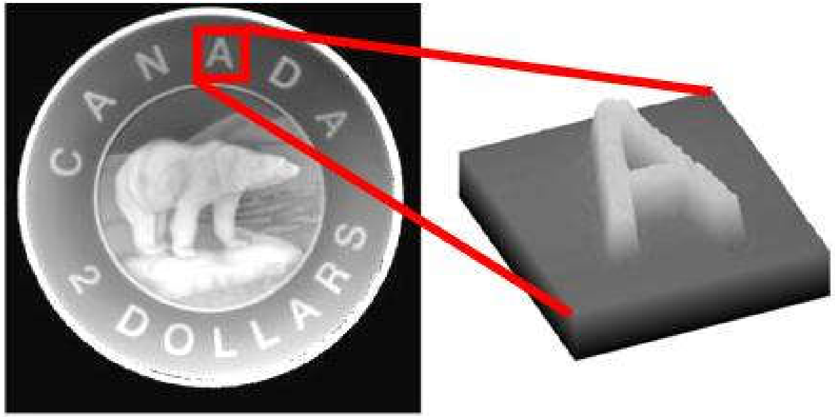
- **Profilometer (non-contact)**
  - optical scanning
  - measure 3D profile
  - spatial resolution - wavelength
  - not suitable for absorptive materials



Metrology

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





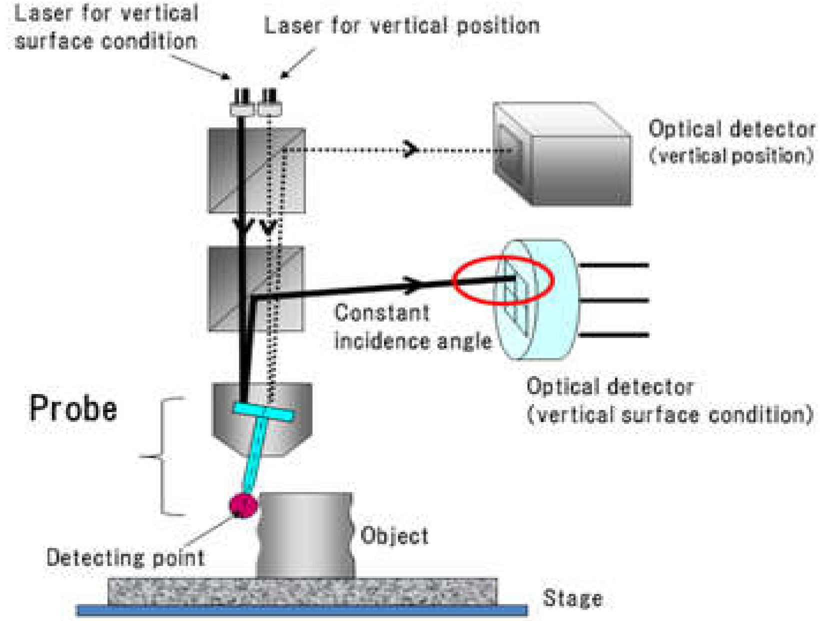
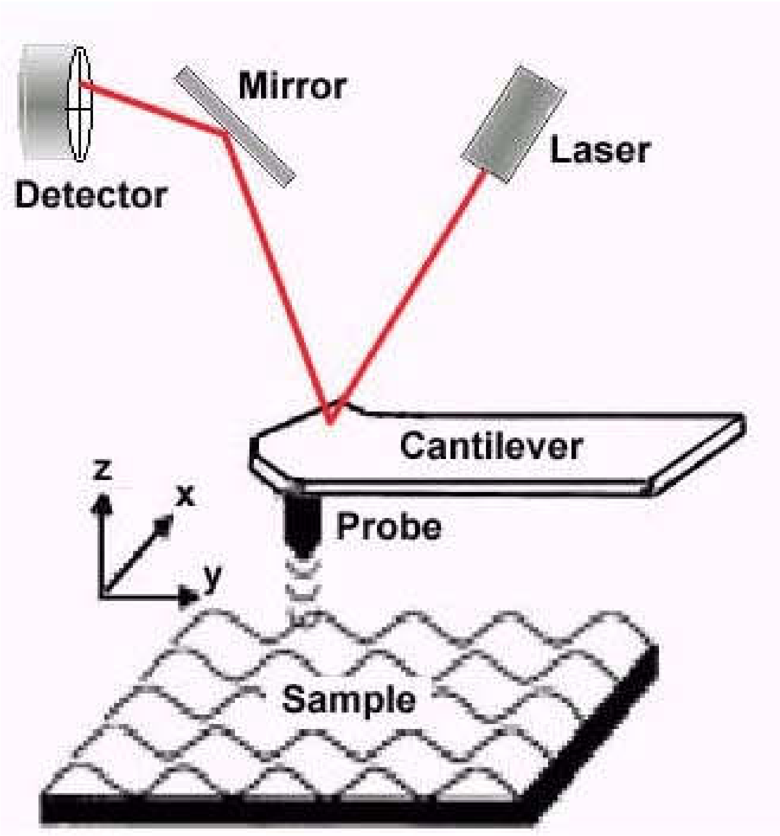
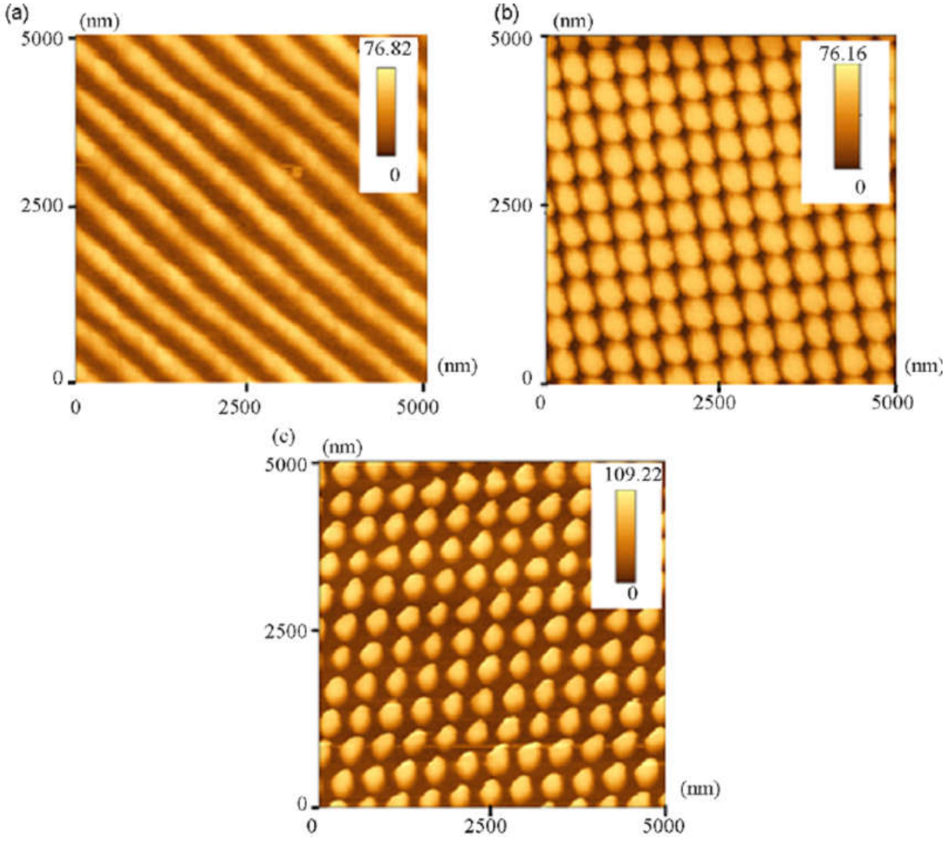


Fig.1 Optical System in Ultrahigh Accurate 3D Profilometer

Metrology

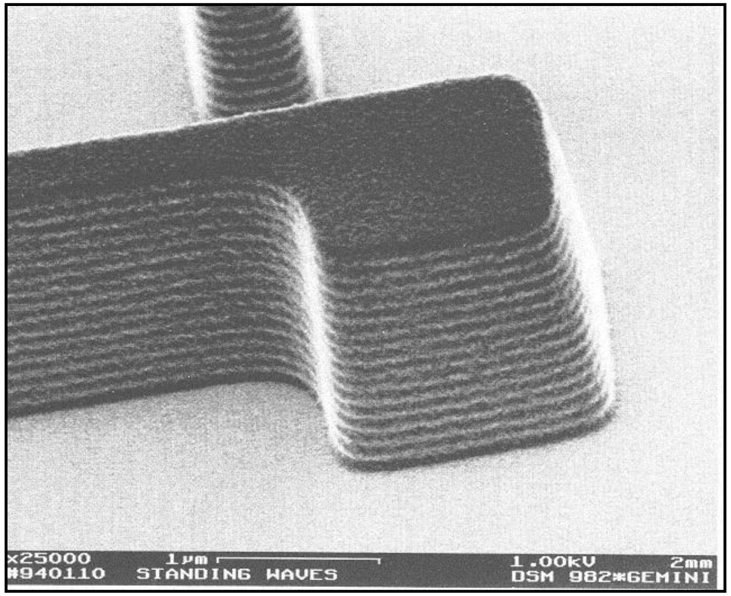
- Atomic force microscope (AFM)
    - better horizontal and vertical resolution

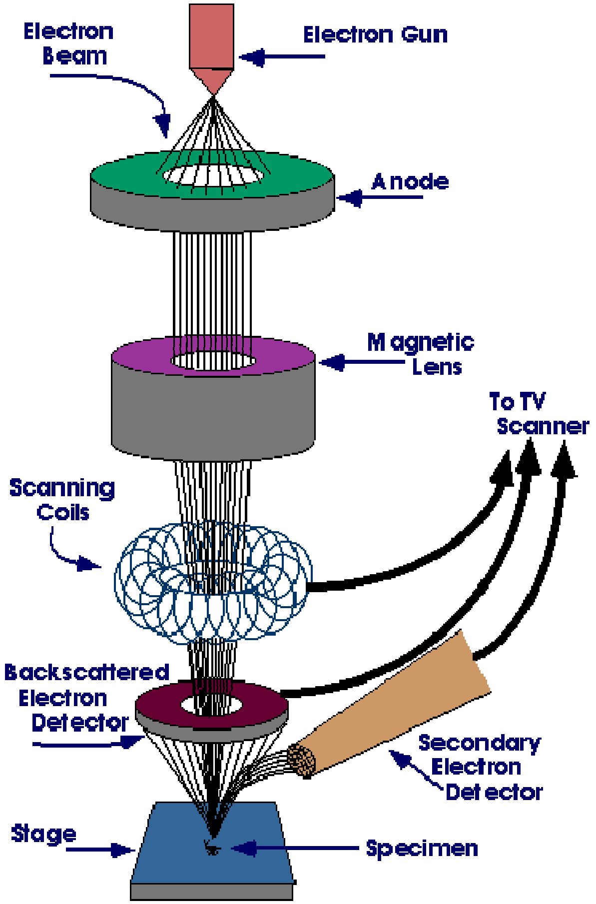




Metrology

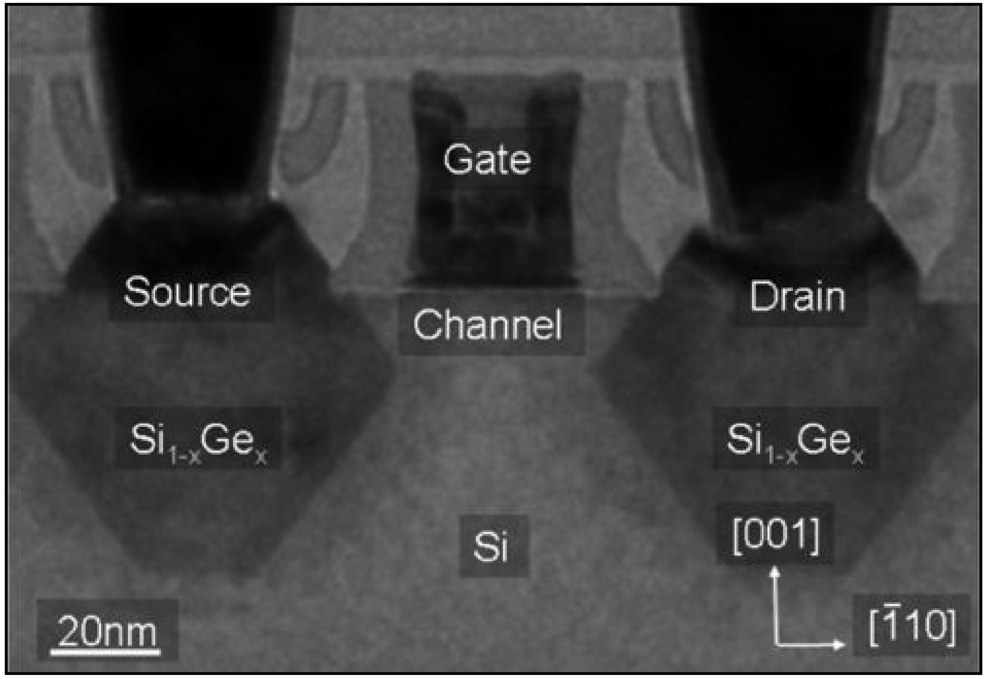
- **Scanning electron microscope (SEM)**
  - ❐ vacuum required
  - ❐ surface charging
  - ❐ can combine with Ebeam lithography

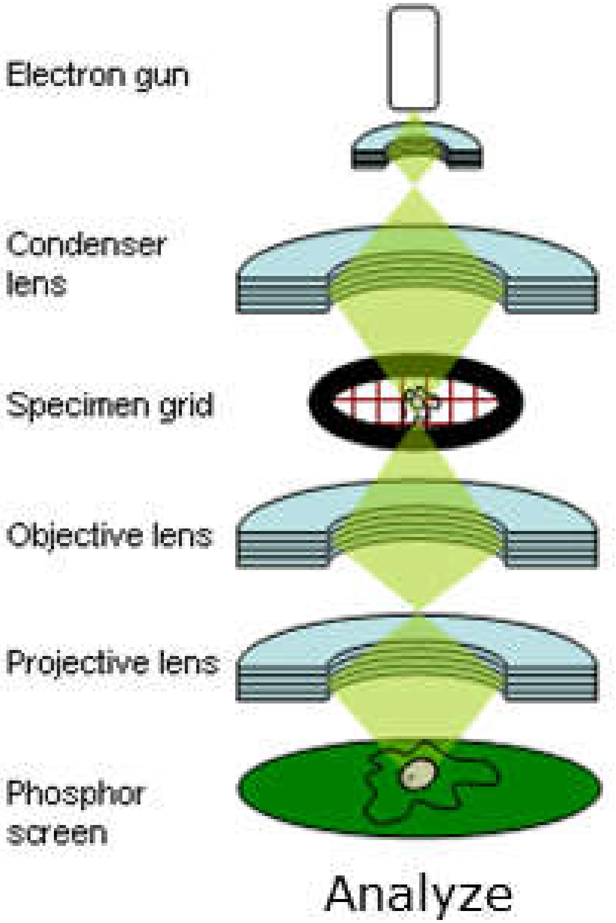




Metrology

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



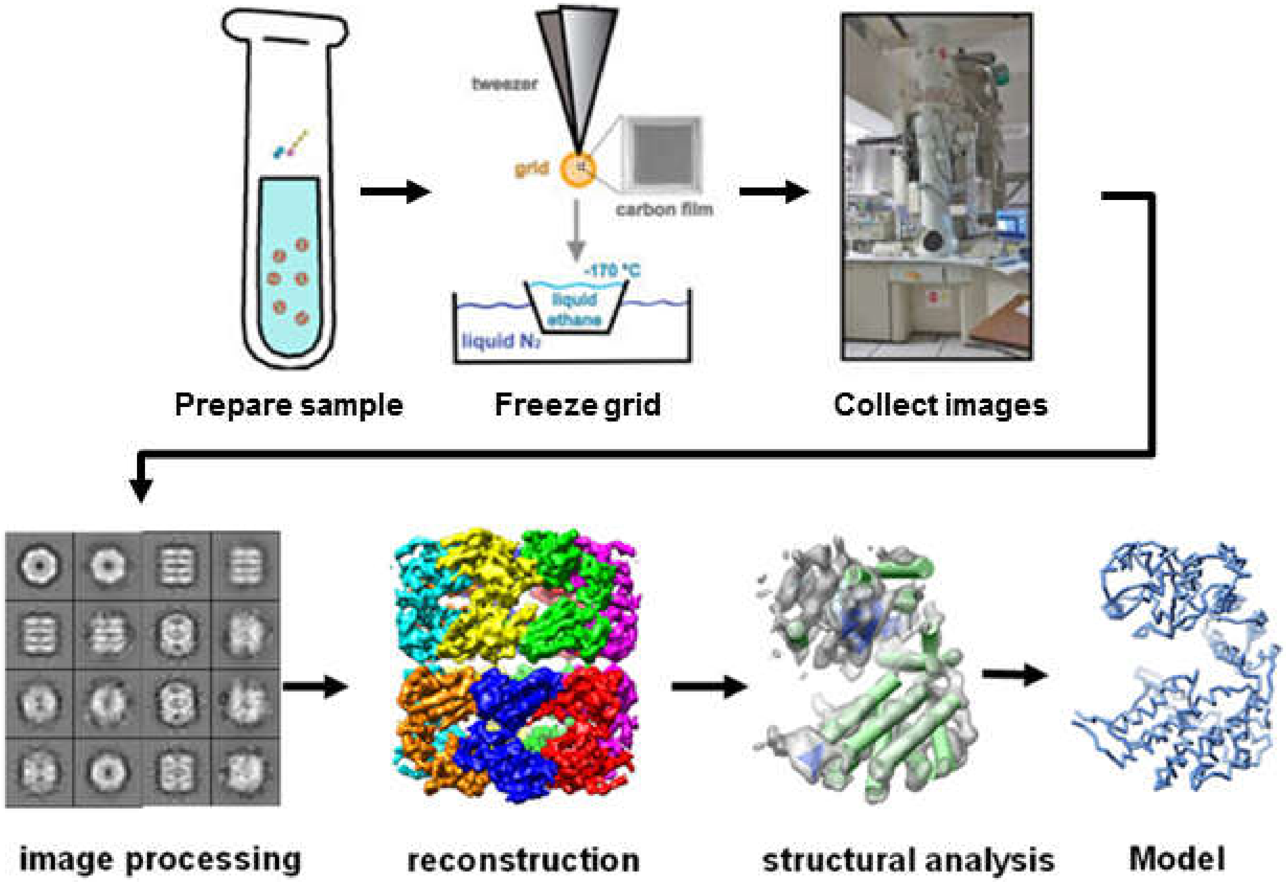


A. Klug
1982 Nobel Prize in Chemistry

E. Ruska
1986 Nobel Prize in Physics

Metrology

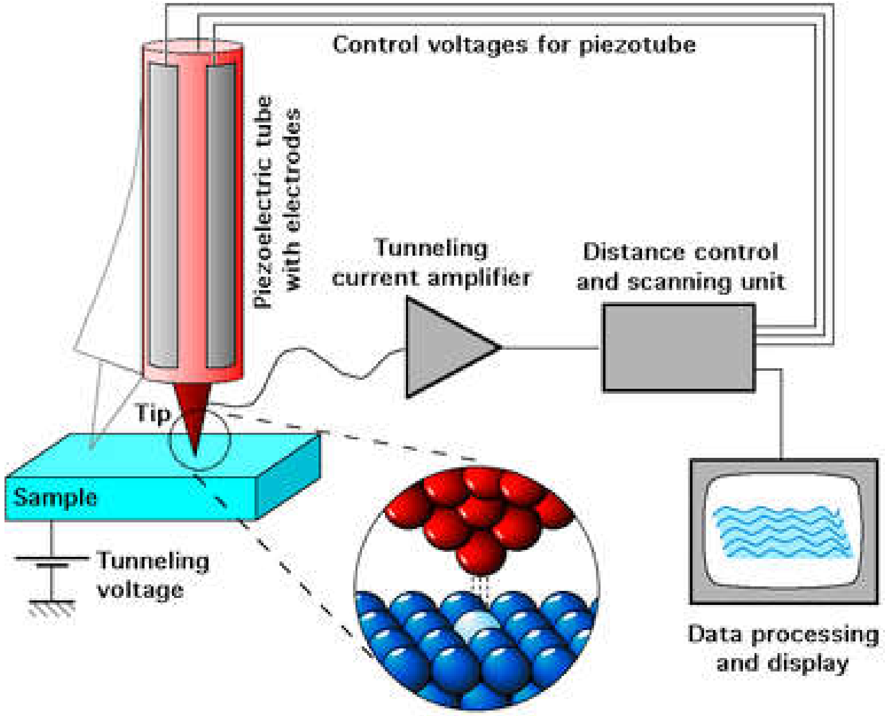
- **cryo electron microscope (cryo-EM)**
  - **image biological samples!**

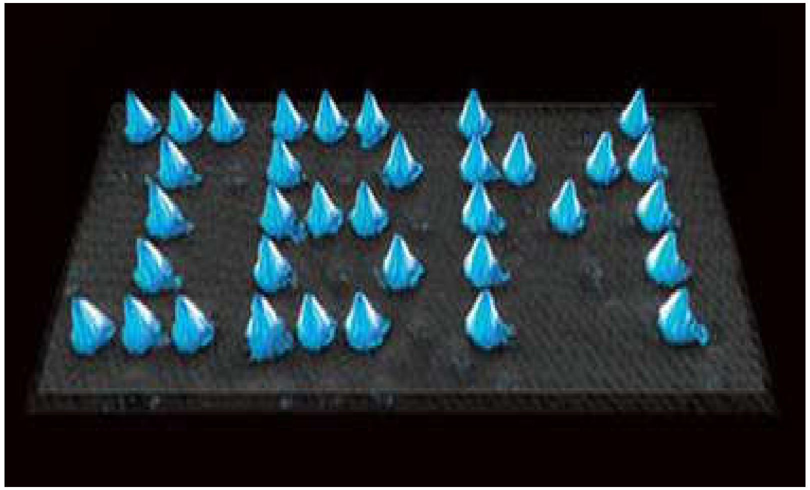


2017 Nobel Prize in Chemistry

Metrology

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





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