Fabrication of nanostructures and nanoscale devices.
Part 5.

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See the lectures at https://www.nanocenter.si/qt-future/education-2/

Parts 5-6, Outline

Principle technological schemes

Difficult choice (device to be discussed on Nov 24)

Part 5 Optical and Electronic Lithography

Polymer and inorganic resists (composition, solubility, microstructure)

Spin-coating, adhesion, roughness

Light and beam interactions with positive and negative resists; amplification

Post-exposure procedures (developers, thermal effects, wetting)

Maskless lithography

Part 6 Assembling of low-dimensional objects

- Dry transfer methods
- Wet transfer methods
- Fabrication of junctions and contacts
- Fabrication of nm-size gaps.

Suggested devices 1: SQUID detectors
(for astrophysics as well)

SQUID is **S**uperconducting **QU**antum **I**nterference **D**evice

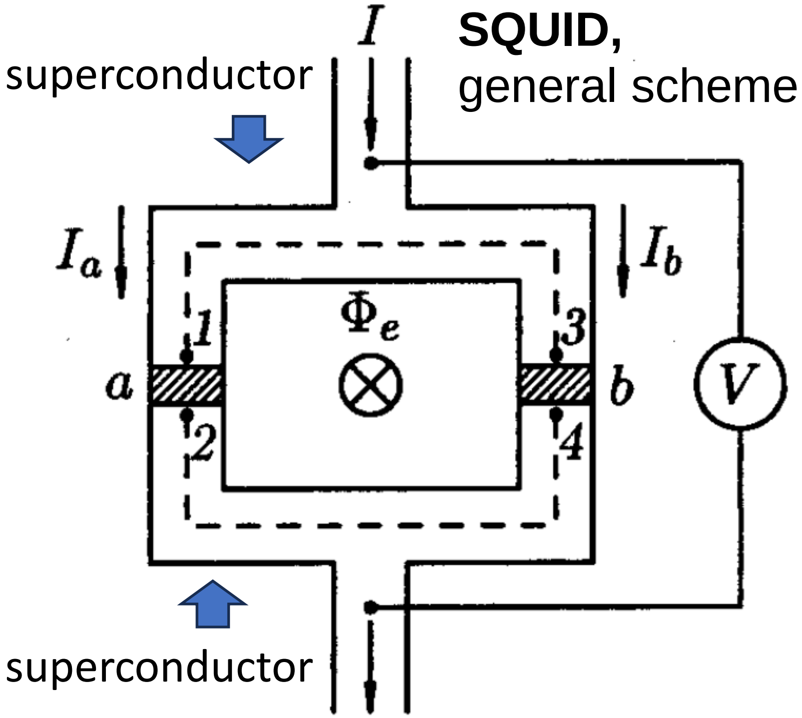
- ✓ DC SQUID: magnetometer (10^{-10} – 10^{-11} Gs); picovoltmeter

- ✓ High-frequency SQUIDs (~ 10 MHz…… 10 GHz)

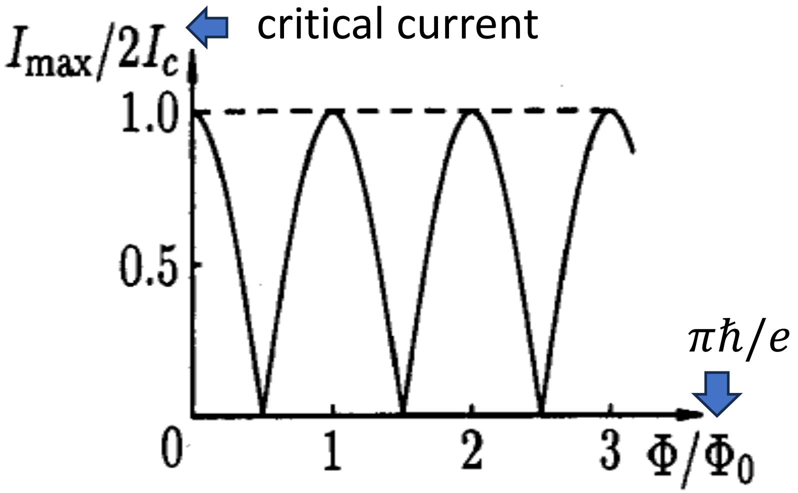
Astro:

Microwave-SQUID **multiplexer** readout, to decrease the number of wires (for microcalorimeters)

DC-SQUID as an **amplifier** for Superconducting Tunnel Junctions



a, b: Josephson junctions
Φ_e: magnetic flux

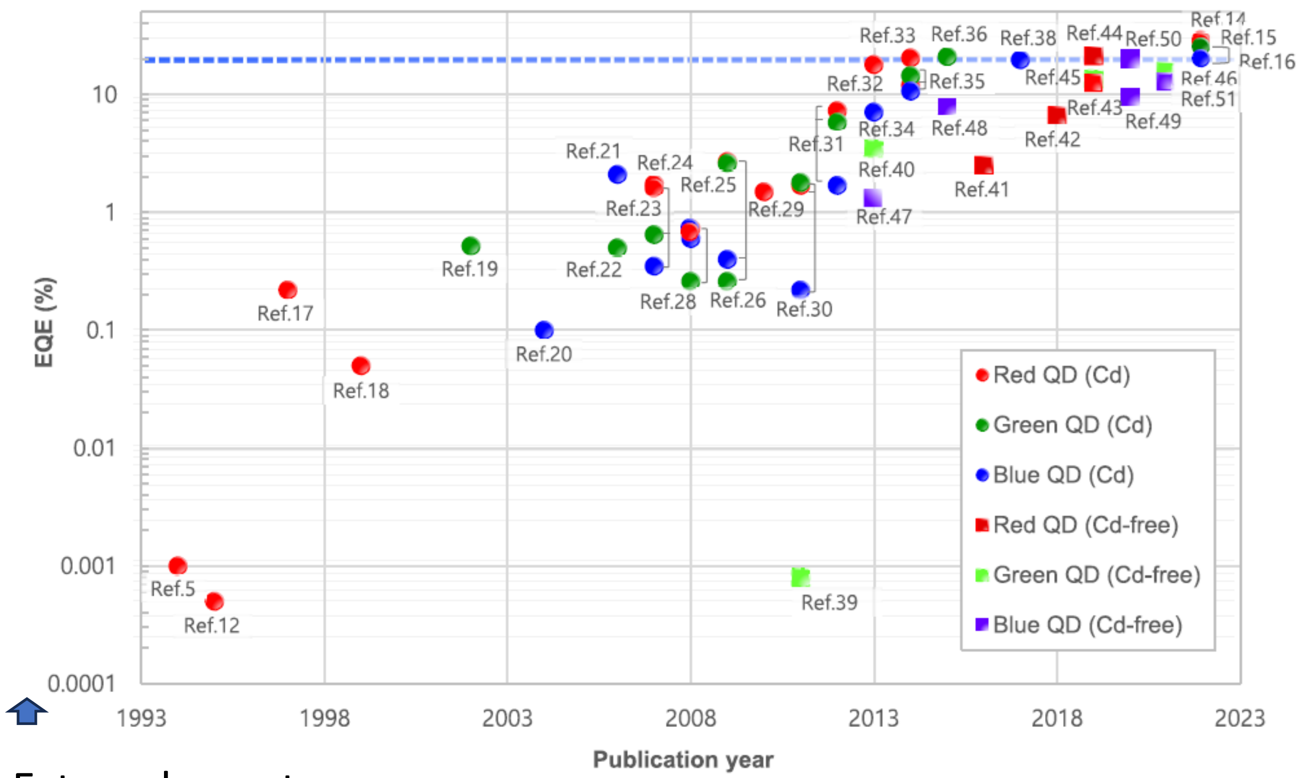


- To consider this type of devices, we should also discuss bolometers, etc.
- This looks more like micro- than like nanotechnology.
- Links to Devices 3 are possible, see * at p.4 below.

See, e.g., IEEE TRANSACTIONS ON APPLIED SUPERCONDUCTIVITY 31 (2021) 1601205 <Simons Observatory>;
Appl.Phys.Lett. 118 (2021) 062601 <1820-channel multiplexer>

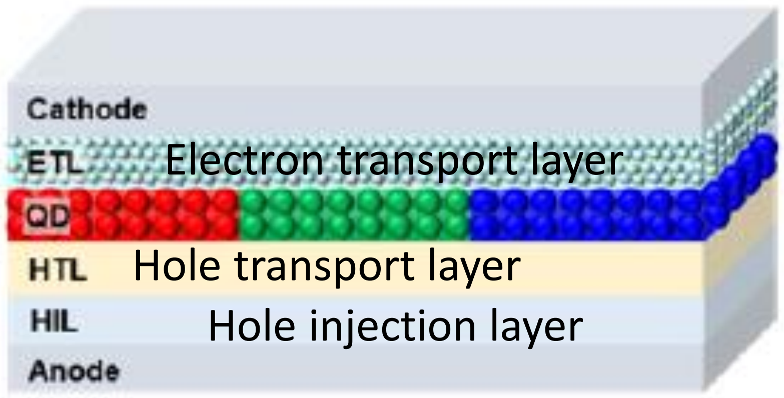
Suggested devices 2: Nanoparticle(QD)-based light-emitting diodes (LEDs)

Citation: «…current methods for fabricating **semiconductor nanoparticle-based** light emitting devices: metal-organic vapor phase epitaxy (MOVPE), fabrication of blue GaN-based LEDs with coating procedures, microfabrication, including mesa etching, metal deposition, lift-off, and annealing.»



External quantum efficiency

QD-LED display



- To consider this type of devices, we should also discuss conducting polymers used in combination with QD.

Chem. Rev. 123 (2023) 4663–4692
Adv. Optical Mater. 11 (2023) No 2201965

Suggested devices 3: Superconducting single photon detectors (SSPD)

Citation: «…ultrathin **films of NbN** onto different substrates (sapphire and MgO) using DC-magnetron sputtering at room temperature - electron beam lithography (EBL) .... generation of single photons from **InAs QDs in GaAs** membrane - applications for detection of broadband light from Cherenkov radiation, scintillation or ionization.»

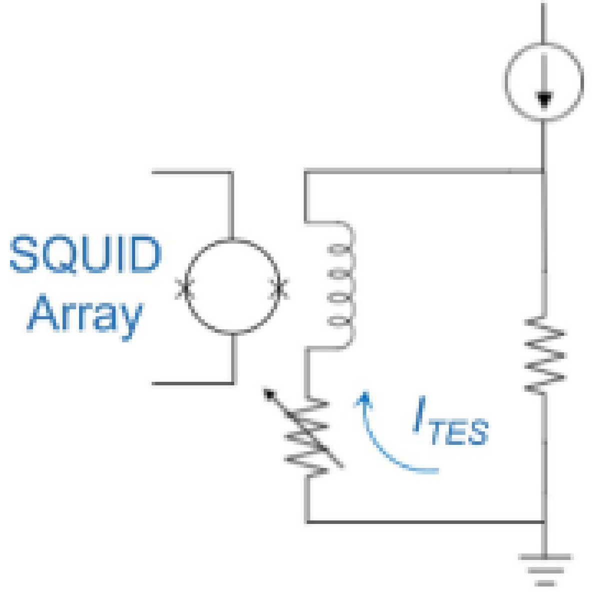
- ✓ Superconducting Tunnel Junctions (STJ, a type of Josephson junction) *
- ✓ Kinetic-Inductance Detector (KID) **
- ✓ Transition-Edge Sensor (TES) (microcalorimeters) *
- ✓ Superconducting Nanowire Single-Photon Detector (SNSPD)

** Intersects with Suggested devices 1, in combination with SQUIDs*

*** Initially developed for astro*

This requires explanations: GaAs waveguides are used in various SSPD; as for QD, they typically present an object, not device (e.g., QD emission can be studied using SSPD).

Or probably some single-photon transistor was assumed?



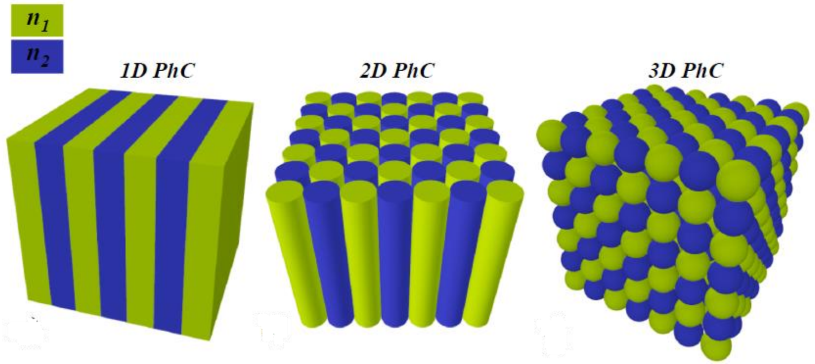
J. Lightwave Technol. 40 (2023) 7578-7597 <various types>

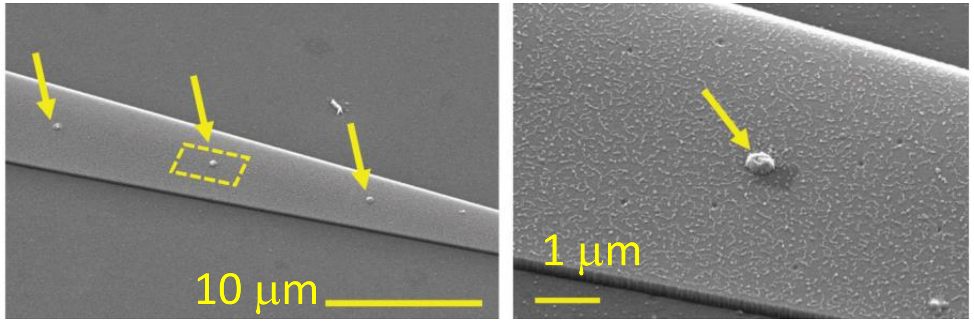
Optical Engineering 53 (2014) 081907 <based on superconducting nanowires>

Suggested devices 4: ‘Photonics and non-linear optics‘ section, three options

Photonic crystals (PhC): this is not a device, but a sort of (meta)material. Devices based on photonic crystals can be light filters, highly reflective mirrors, waveguides, polarizers, etc. It is important to agree dimensions:

Optics & Laser Technology 142 (2021) No 107265





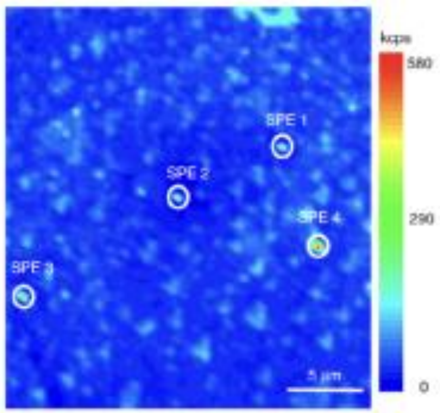
Quantum micro resonators: consider the most usual version of ring resonators with QD,

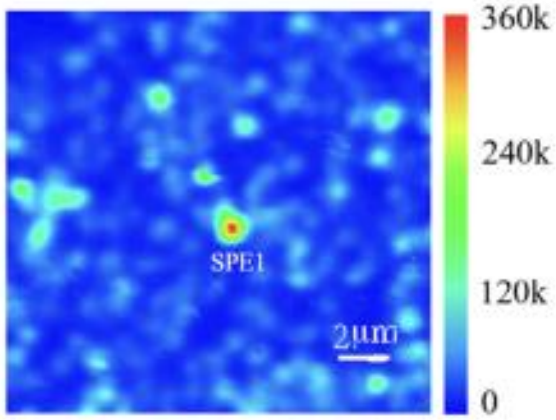
see example in Nanophotonics 9 (2020) 1411–1423

Single-photon sources: essentially different types are

- single emitters (mostly 1D objects, like QD, or molecules),
- based on excitations in atomic ensembles (more rare),
- based on correlated pairs of photons.

Rev. Sci. Instrum. 82 (2011) No 071101
Quantum Information Processing 22 (2023) No 360



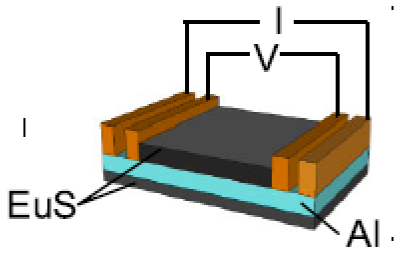


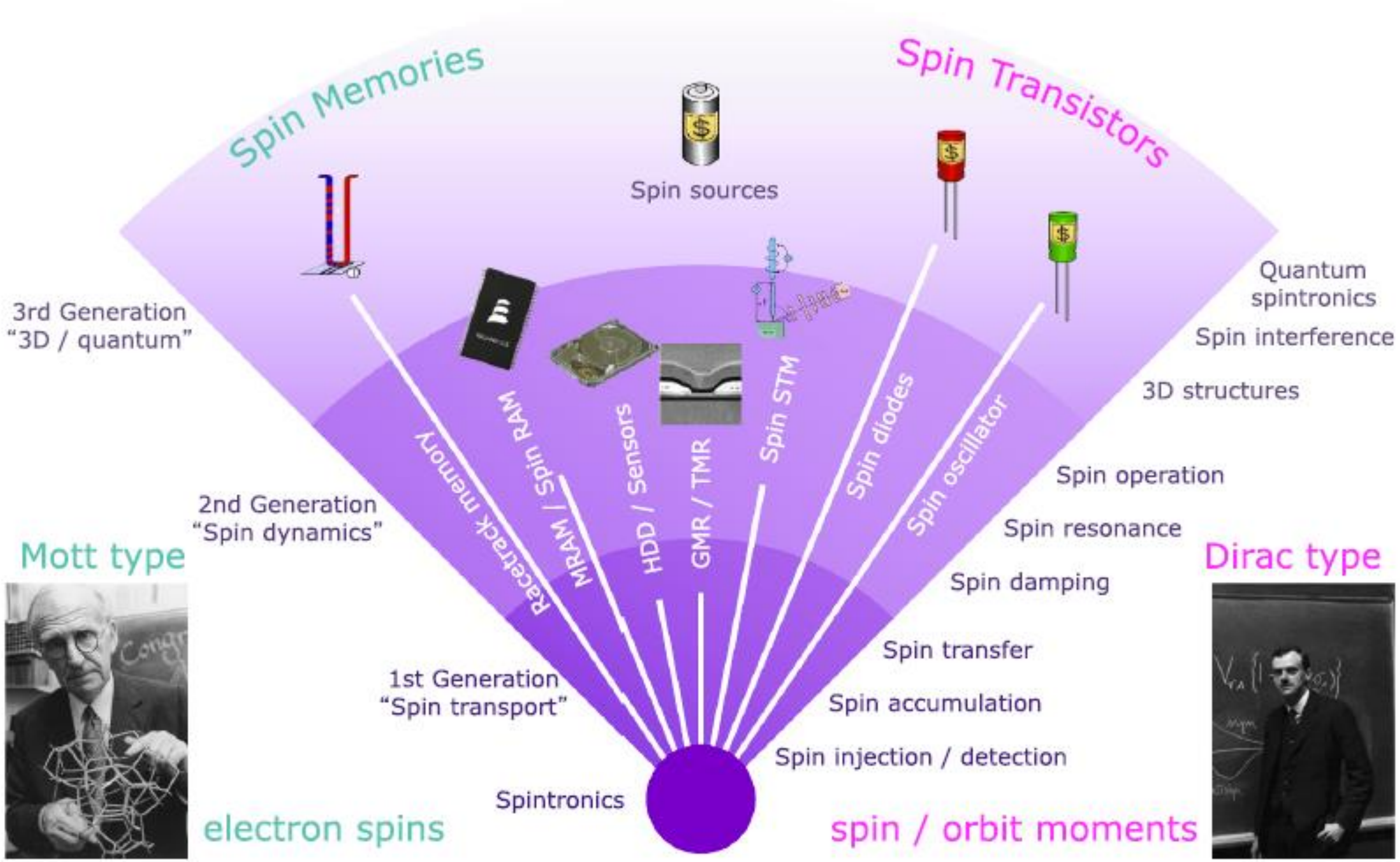
Interesting is a possibility to apply point defects as 1D emitters (SiC at the left, GaN at the right)

Suggested devices 5: Spintronics

Citation: «… spin valve, giant magnetoresistance, spin-transfer torque in magnetic tunnel junctions, ...), monolithic spintronics (single spin logic devices), hybrids like spin-(MOS)FETs, carbon-based spintronics, maybe to mention magnetic skyrmions, ... It would be in general interesting to make an overview of nanoelectronic devices and connect them with already mentioned fabrication techniques and materials that are proposed/used in their fabrication.»

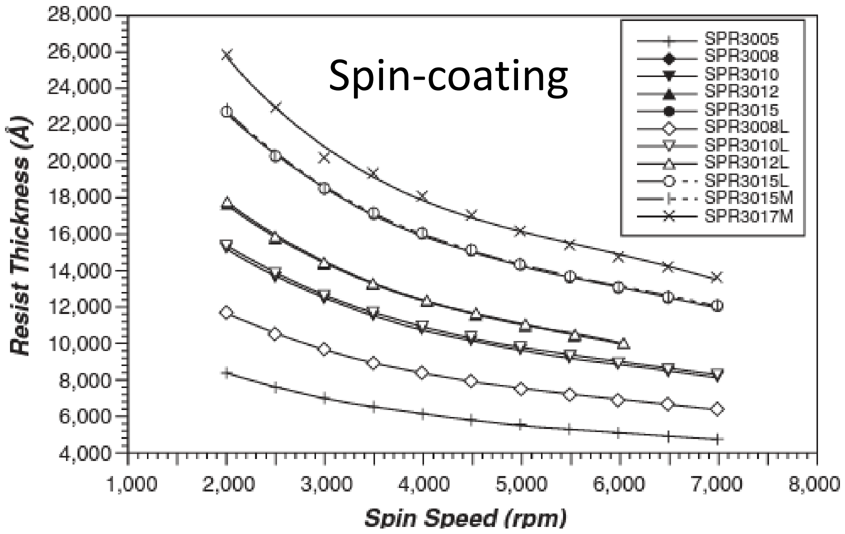
This list contains both phenomena and devices, which should be separated. E.g., spin valve can be based on GMR phenomenon, as well as on the junction of ferromagnetic insulator and superconductor:

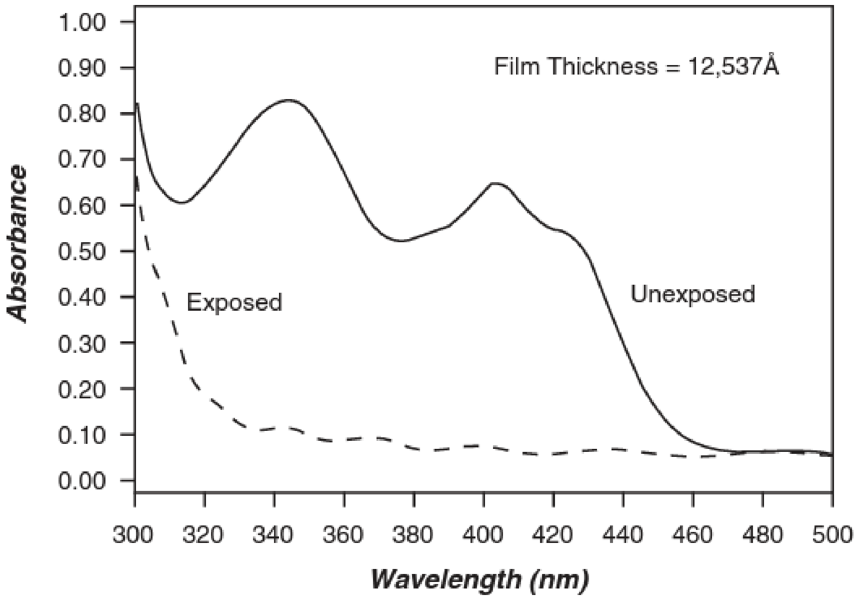


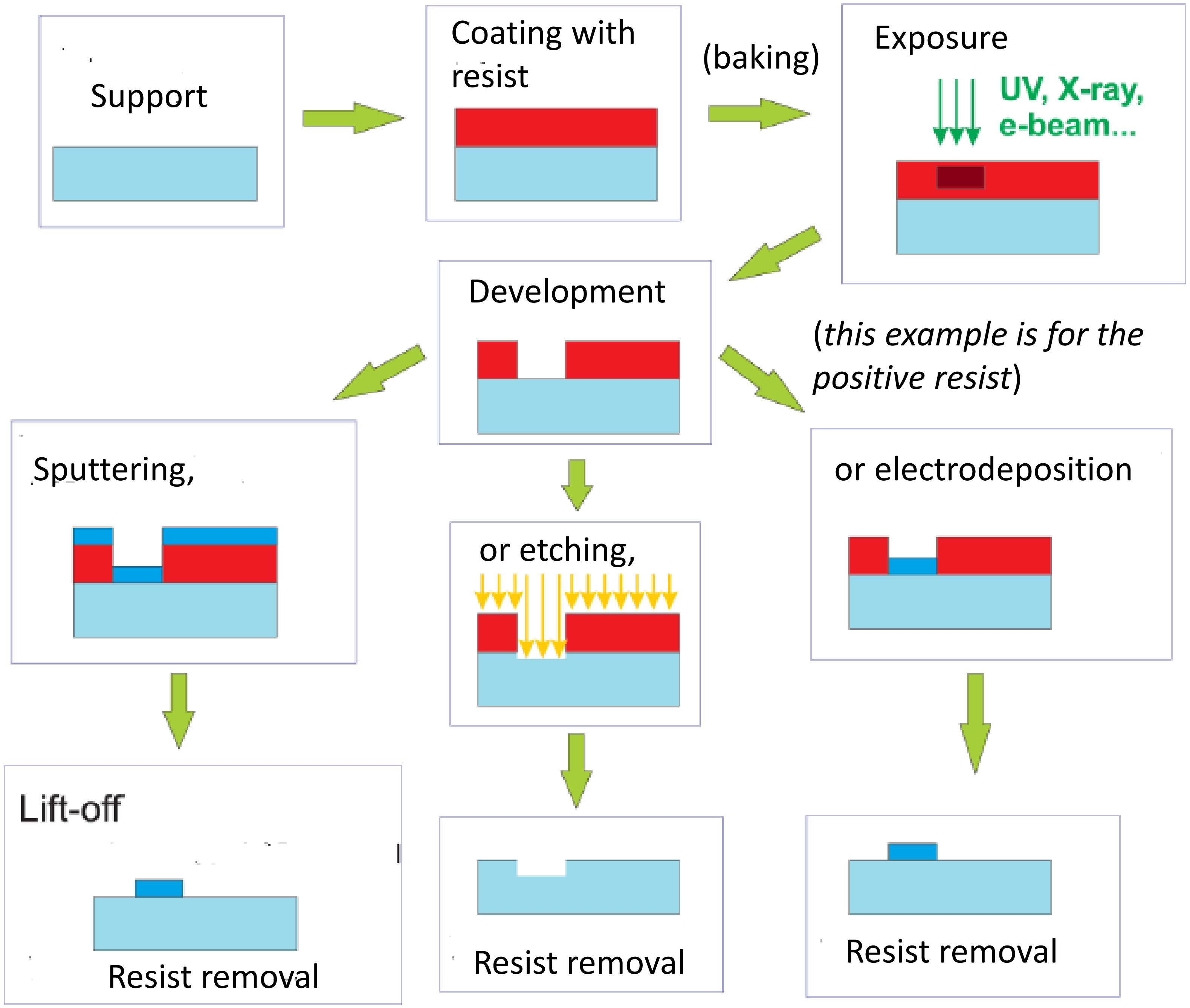


Please, try to make selection from, to say,
J. Magnetism Magnetic Mater. 509 (2020) No 166711

Lithography, general scheme

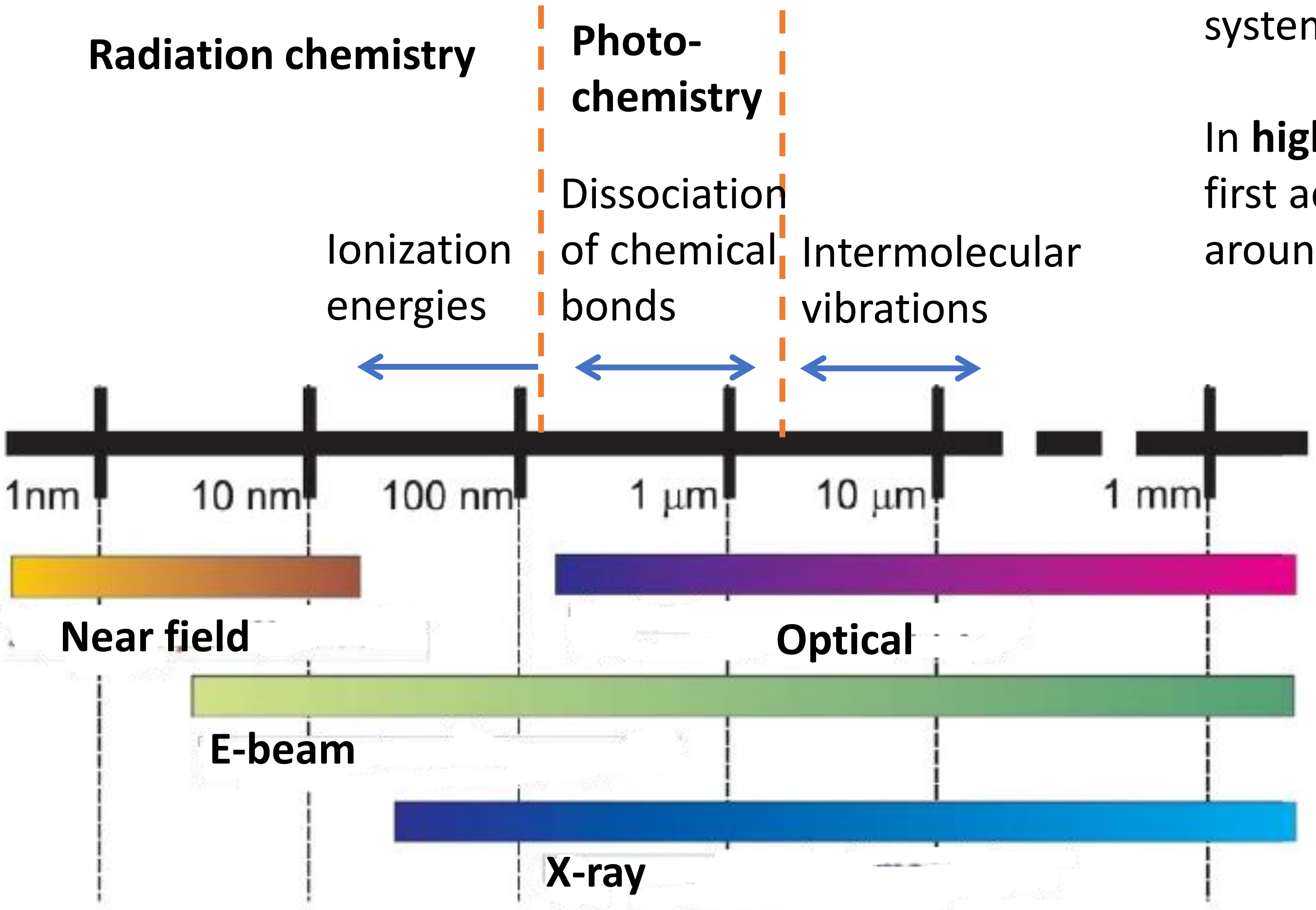






https://kayakuam.com

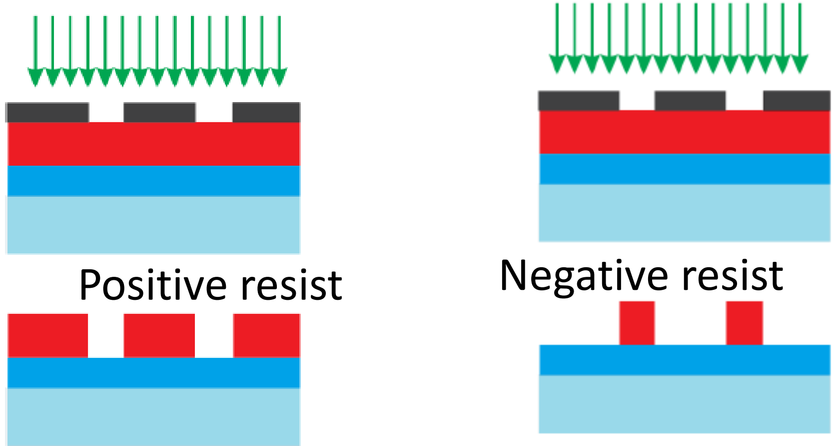
Resolution (size of the micro/nanostructure fragments) and characteristic energy for high energy chemical events



Usual **'thermal' chemistry** operates with the energies of the order of kT. Energy is transferred to macroscopic system and distributed statistically between molecules.

In **high energy chemistry**, large portions of energy are first accepted by single molecules, and then sticks around.

Resists are the polymers which undergo photochemical or e-beam induced transformation, which increase (positive) or decrease (negative) their solubility:



Polymers

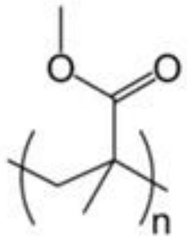
Polymerization degree ***n*** is
a number of monomers.

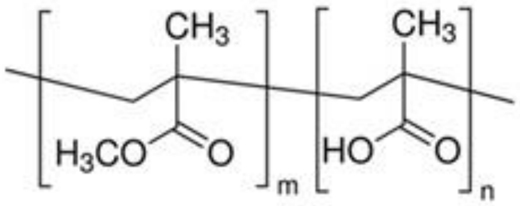
Polydispersity index (PDI) is the ratio of average numerical and average mass molecular weights.

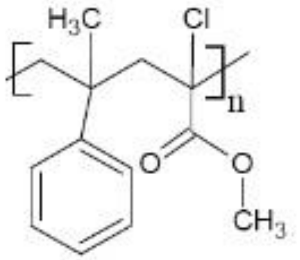
Homopolymer – the chain consists of identical units (monomers)

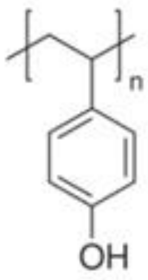
Co-polymer – various monomers are located one by one

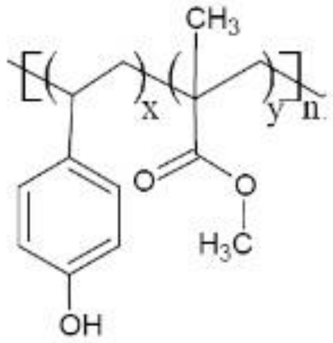
Block co-polymers – repeated blocks of various monomers

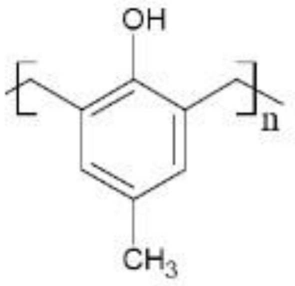


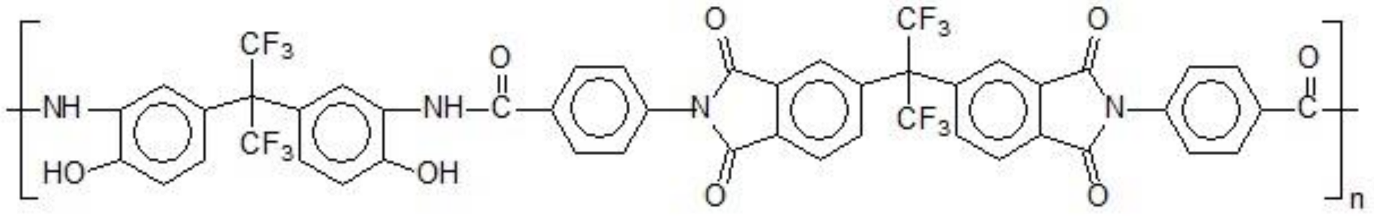


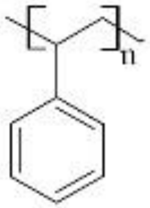








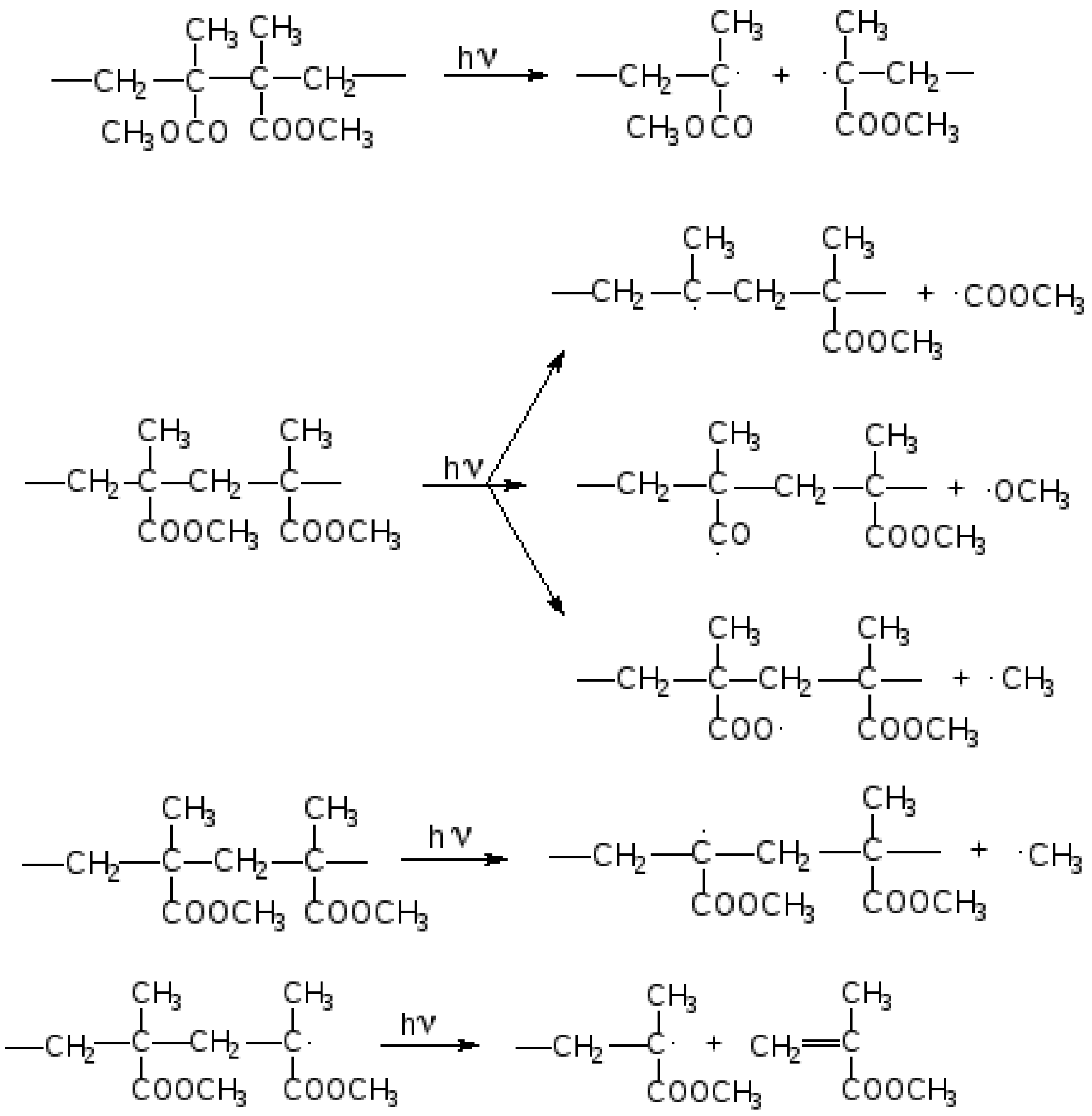




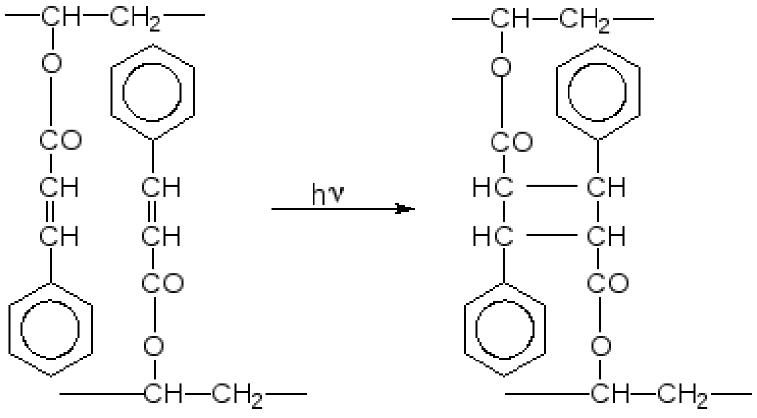
Introductory textbook: Sebastiao V. Canevarolo, Jr., Polymer Science. *A Textbook for Engineers and Technologists*. Elsevier, 2020

Typical transformations of polymers under irradiation

Positive resists



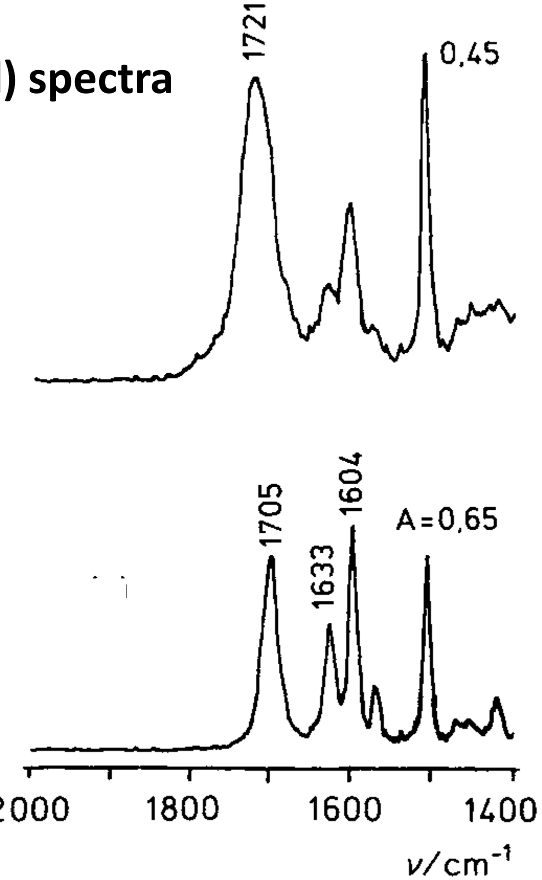
Negative resists



IR (vibrational) spectra

Before exposure

After exposure

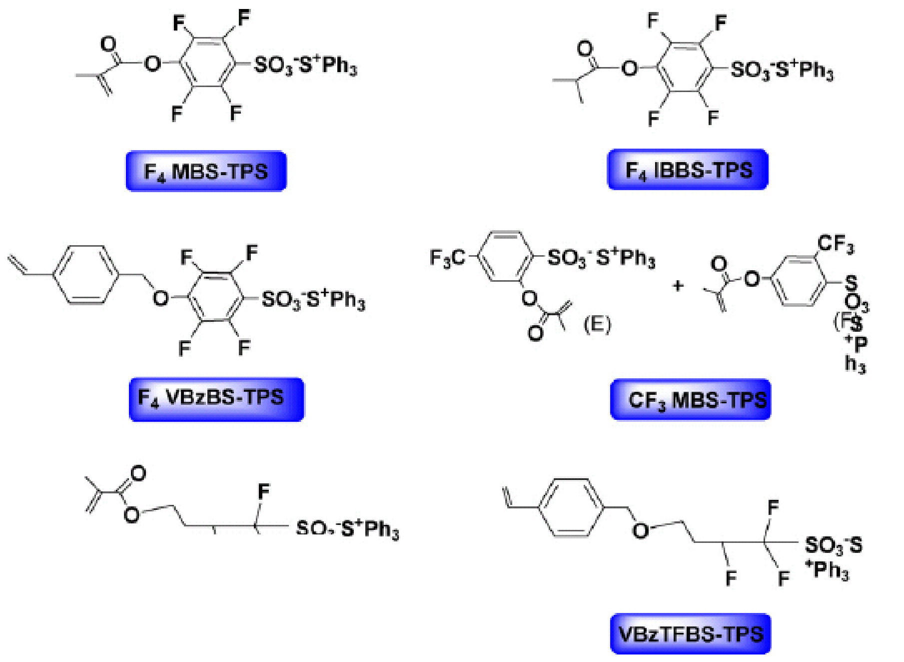


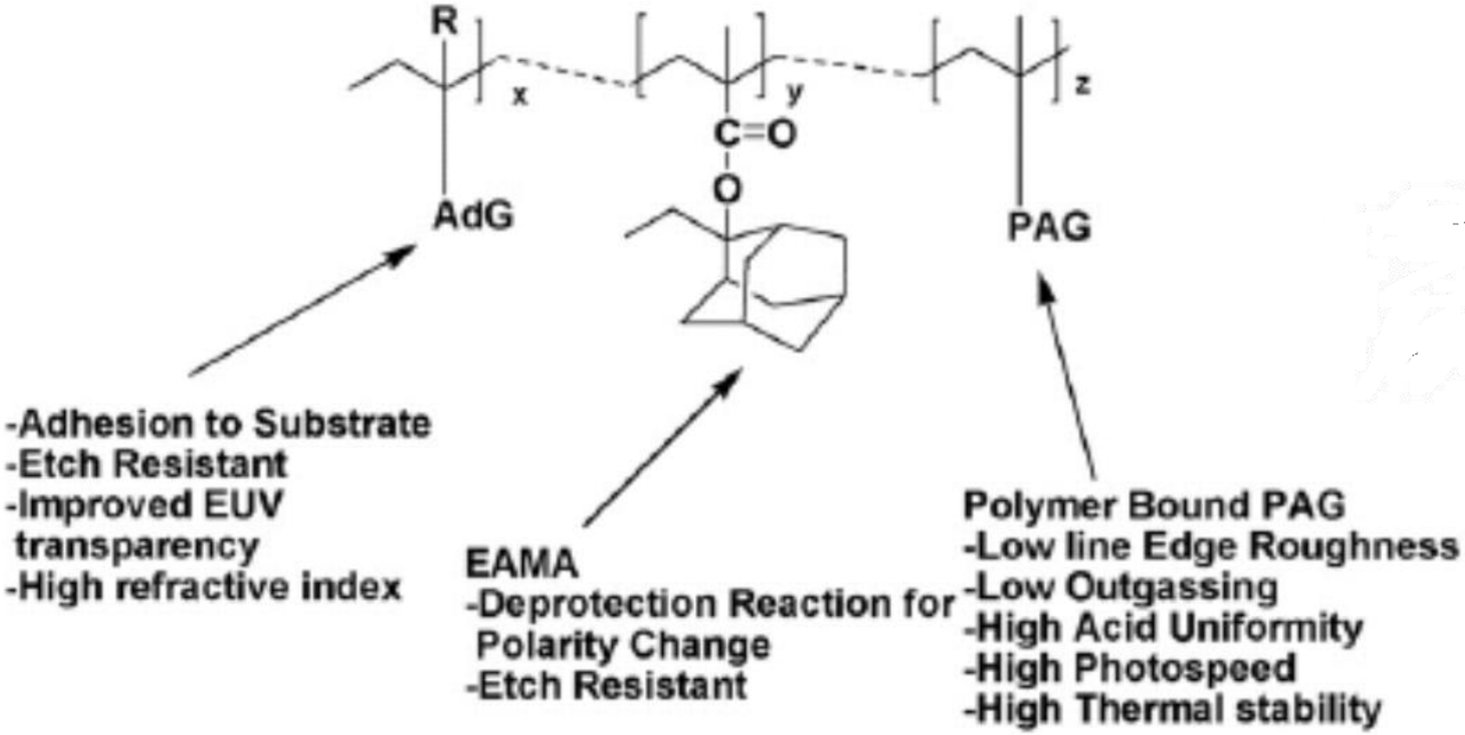
Makromol. Chem. Rapid Commun. 10 (1989) 391

Chemically amplified resist (CAR)

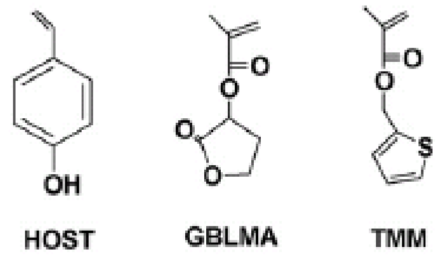
Photoacid generator (PAG)

Can be dissolved or bonded to the polymer chain.





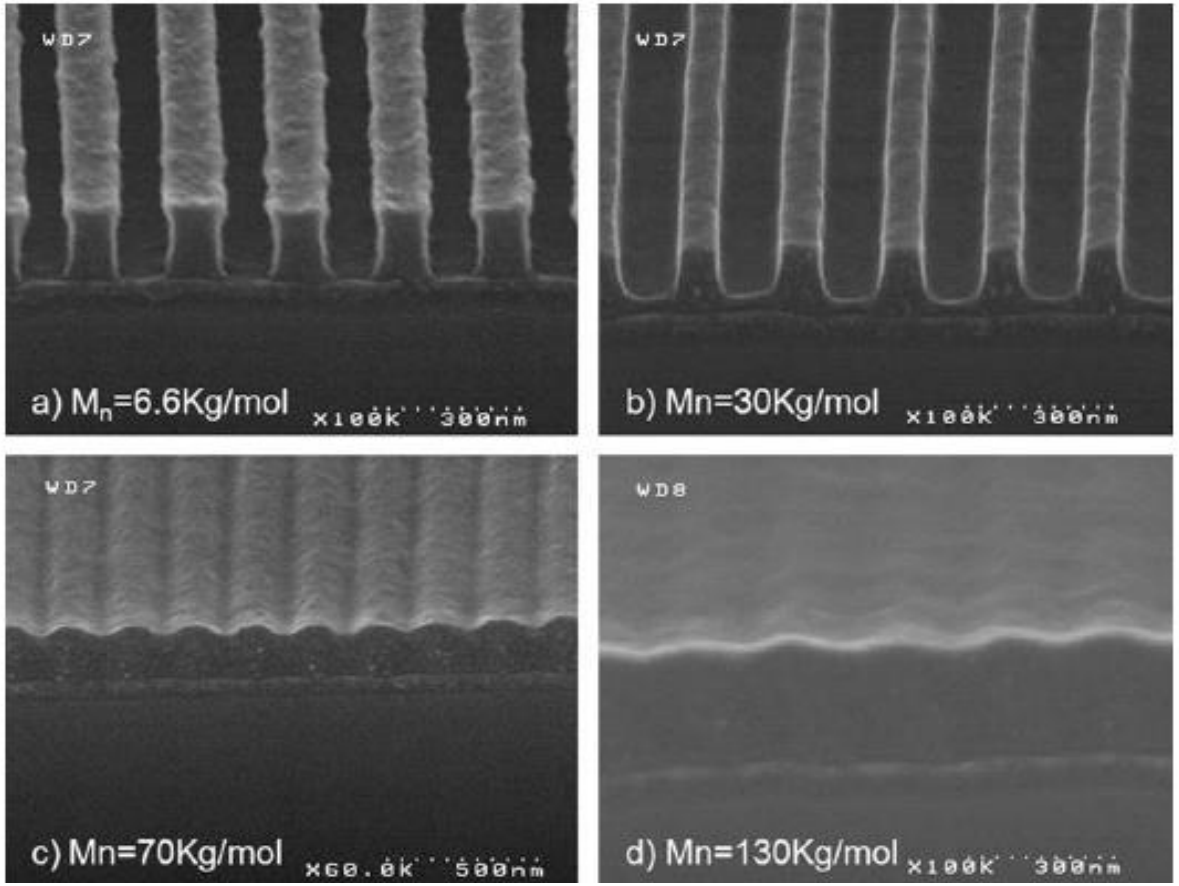
Functional groups which improve adhesion



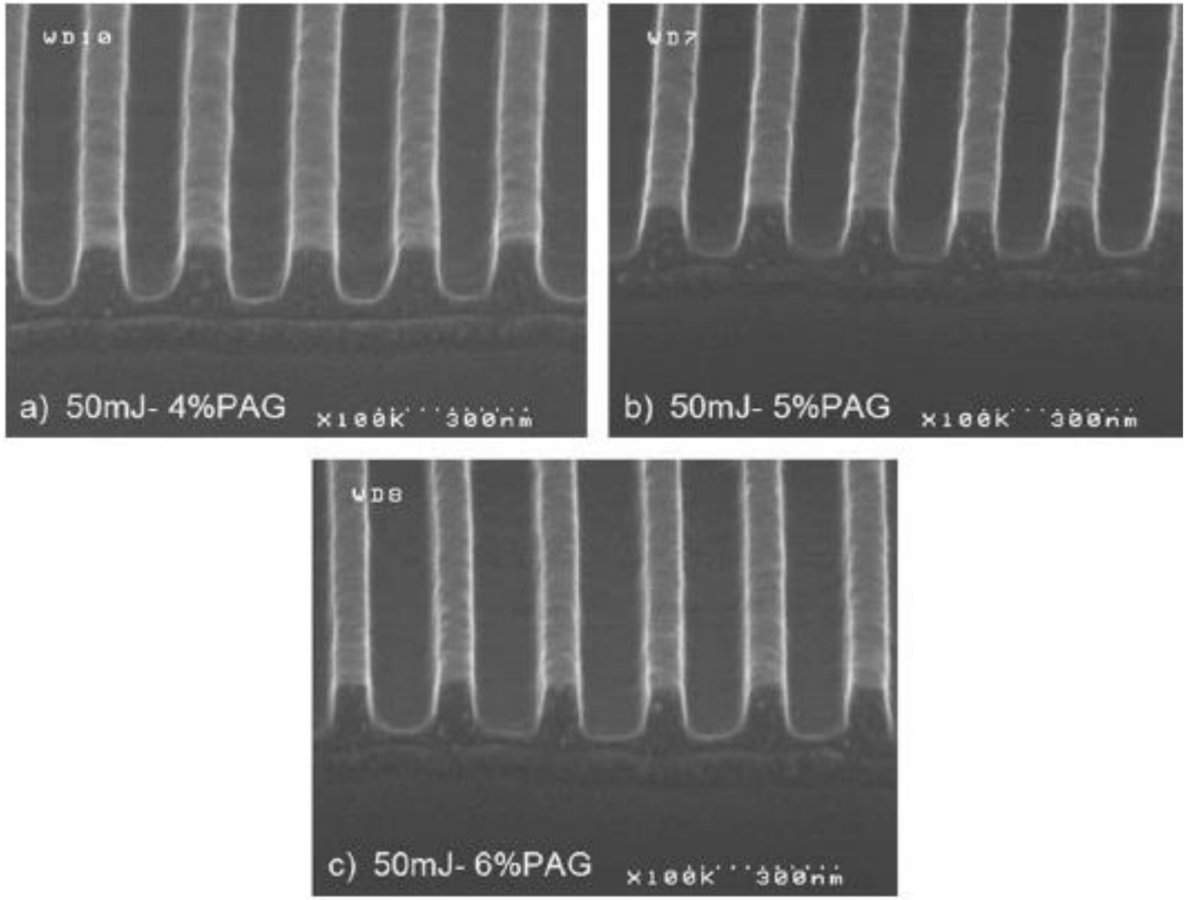
J. Fluorine Chem. 129 (2008) 607

Empiric optimization

Molecular weight, 6.6 … 130 kg/mol

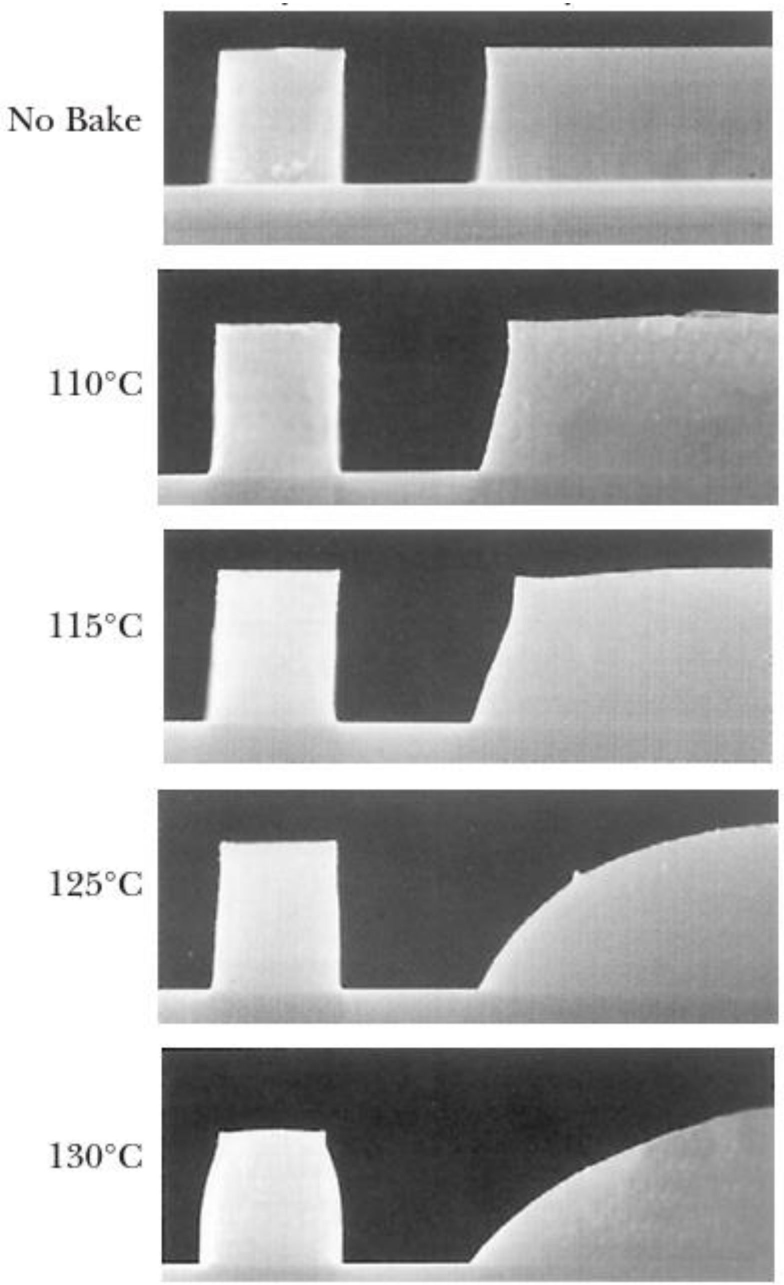


PAG content, 4 … 6 %



Microelectronic Eng. 86 (2009) 796

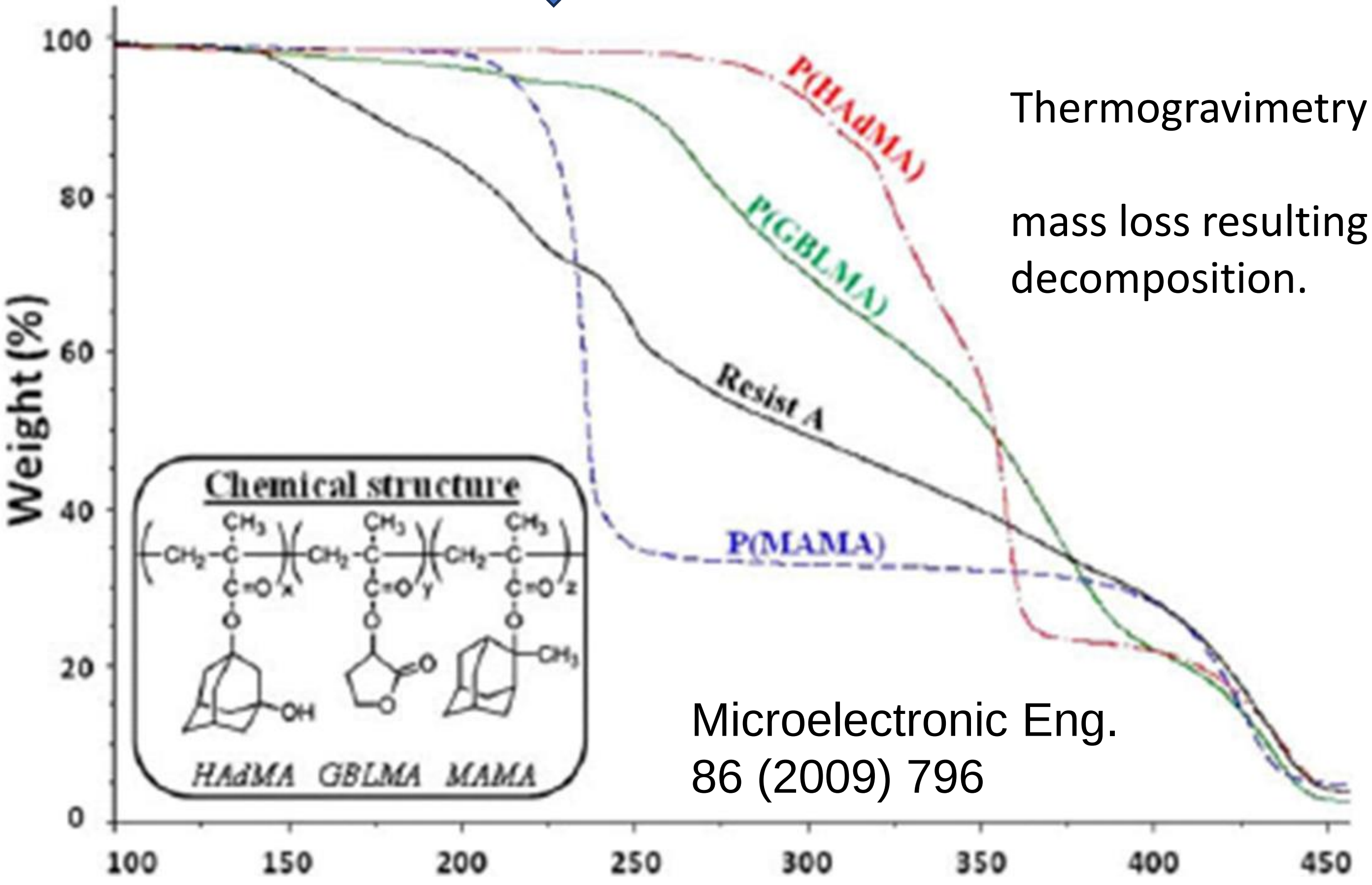
Thermal behavior of polymers



SPR3000 series,
https://kayakuam.com

Melting starts from transition to glass state.

Further increase of temperature results in chemical decomposition.



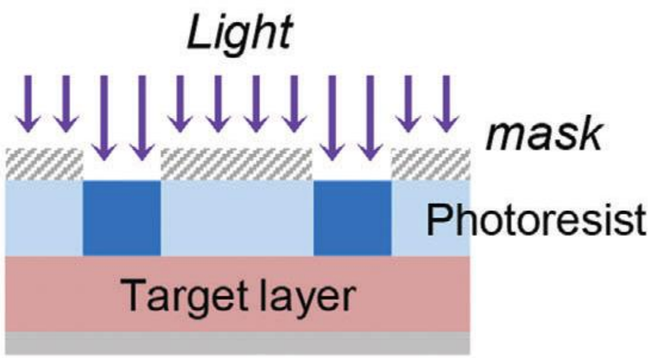
Temperature, C

Microelectronic Eng.
86 (2009) 796

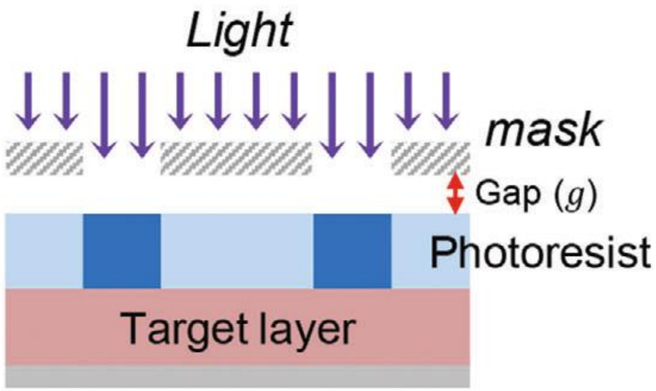
Thermogravimetry (TG):

mass loss resulting from decomposition.

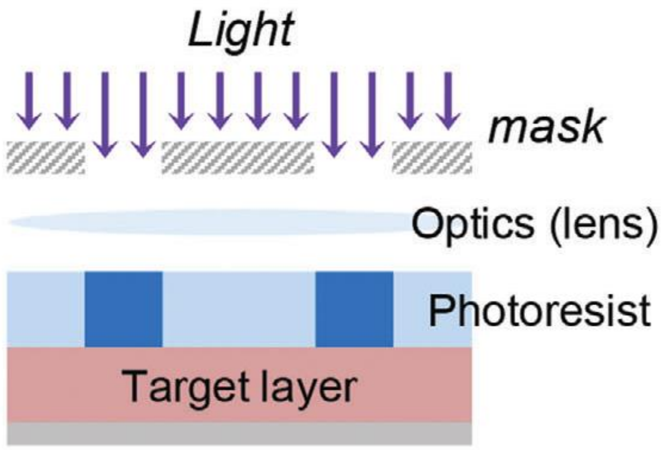
Contact photolithography	Proximity photolithography	Projection photolithography



Risk of contamination

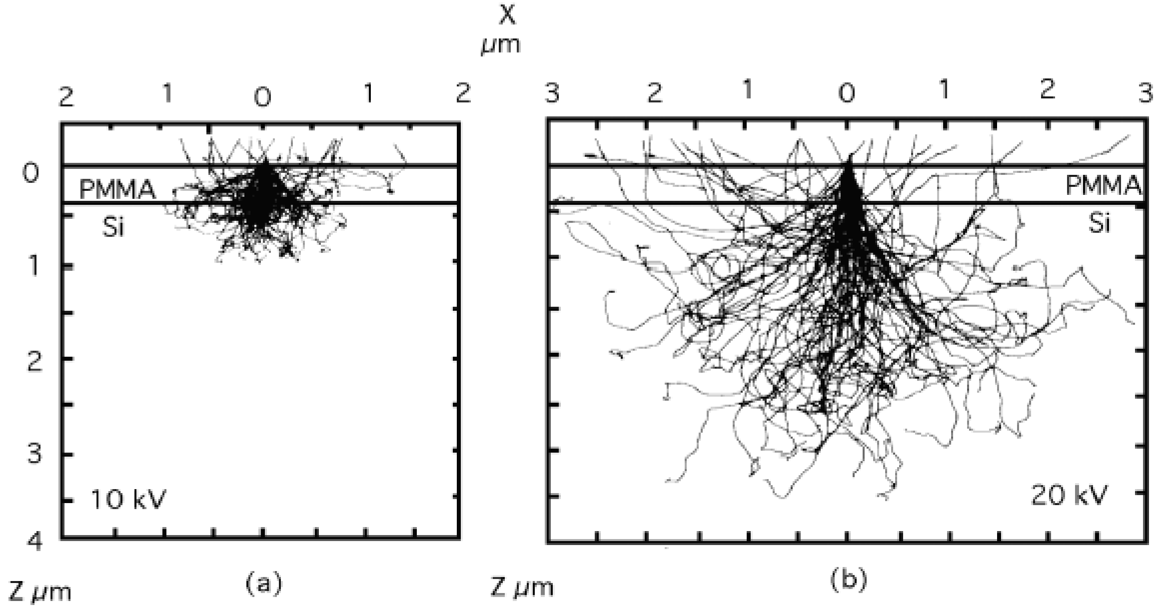


Less desirable diffraction.
Resolution ~ sqrt(λg)



E-beam lithography:

beam scattering results in proximity effects

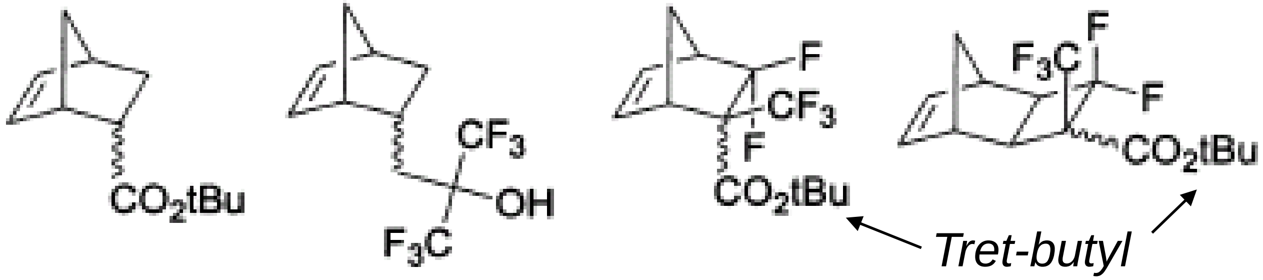


Thin-layer supports

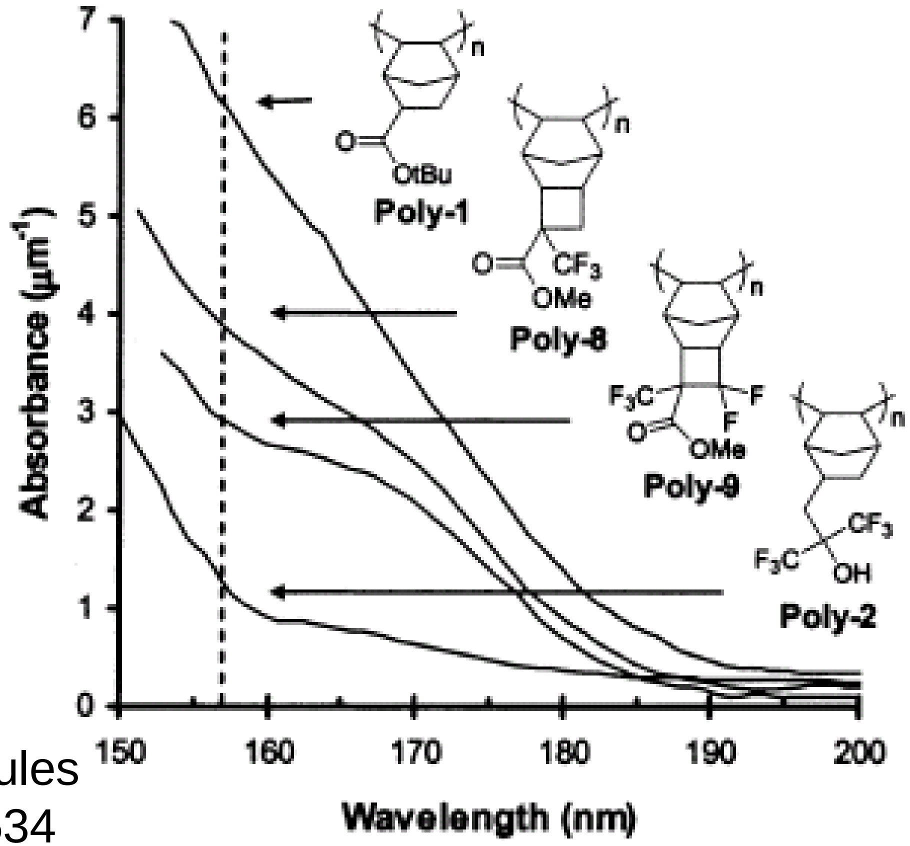
Thin resist layers

Multilayer resists

Low absorbance at short wave length is desirable



Fluor-substituted nonbornene polymers

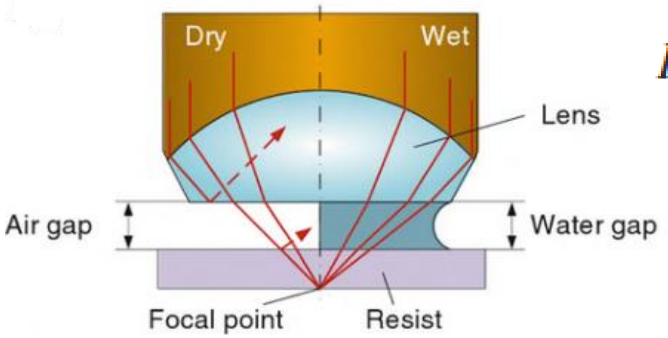


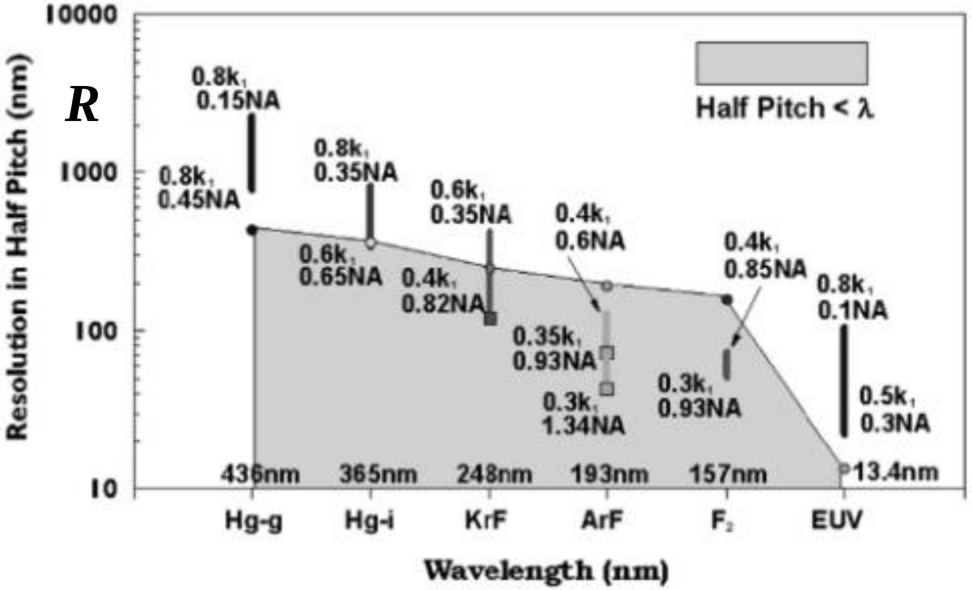
Macromolecules
36 (2003) 1534

Numerical aperture increase: immersion lithography

Rayleigh equation:

$$R = k_1 \frac{\lambda_0}{n \cdot \sin\theta}$$



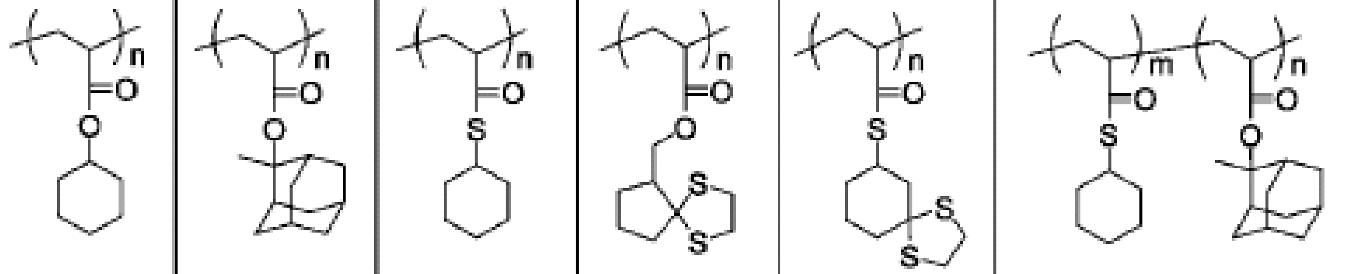


Chem. Rev. 110 (2011) 321

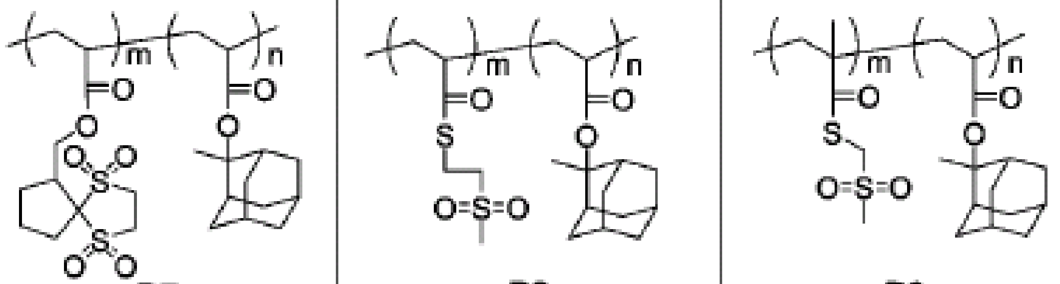
Requirements to resists for immersion lithography

High refractive index: S-containing polymers

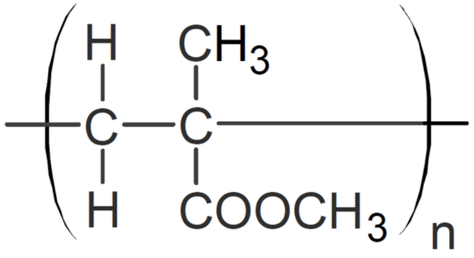
193 nm



	P1	P2	P3	P4	P5	P6
n_{193}	1.66	1.73	1.84	1.84	1.94	1.78
Abs_{193} (mm^{-1})	0.08	0.13	3.15	3.28	5.29	1.19
S (wt%)	0	0	18.8	26.2	36.9	8.2

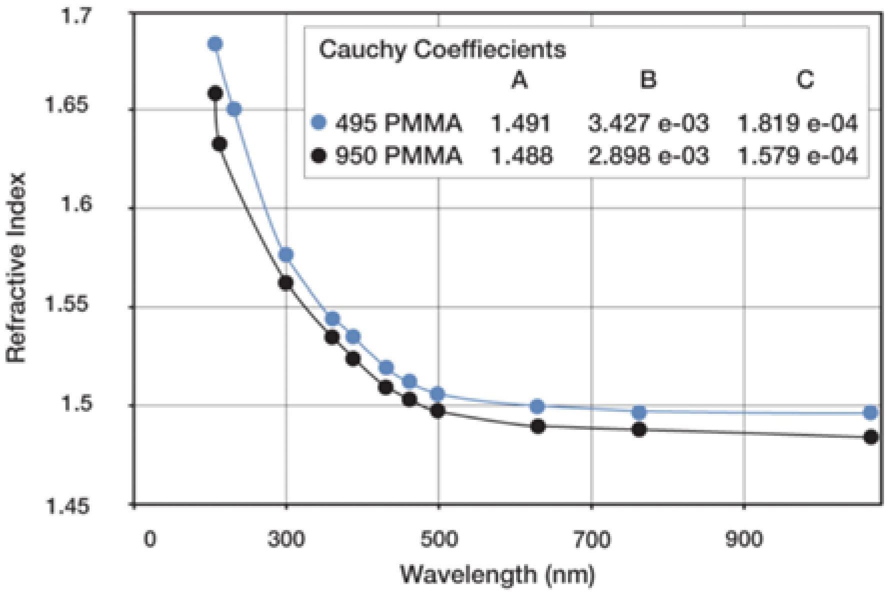


	P7	P8	P9
n_{193}	1.74	1.82	1.81
Abs_{193} (mm^{-1})	0.17	1.25	1.32
S (wt%)	12.1	15.5	15.5



Polymethyl methacrylate: PMMA

Usual PMMA resist, for comparison

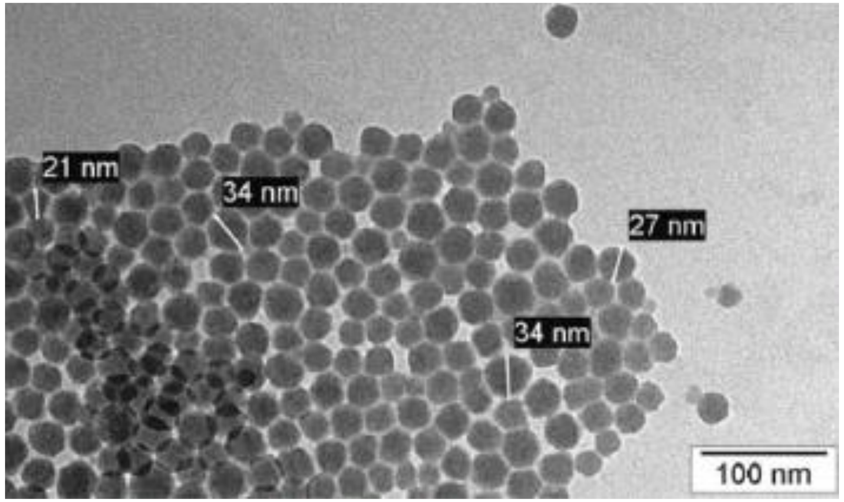


+ low swelling in liquid

Macromolecules 41 (2008) 5674

https://kayakuam.com

'Nanofluids' as a medium for immersion lithography



SiO_2 and ZrO_2 colloid particles can be applied

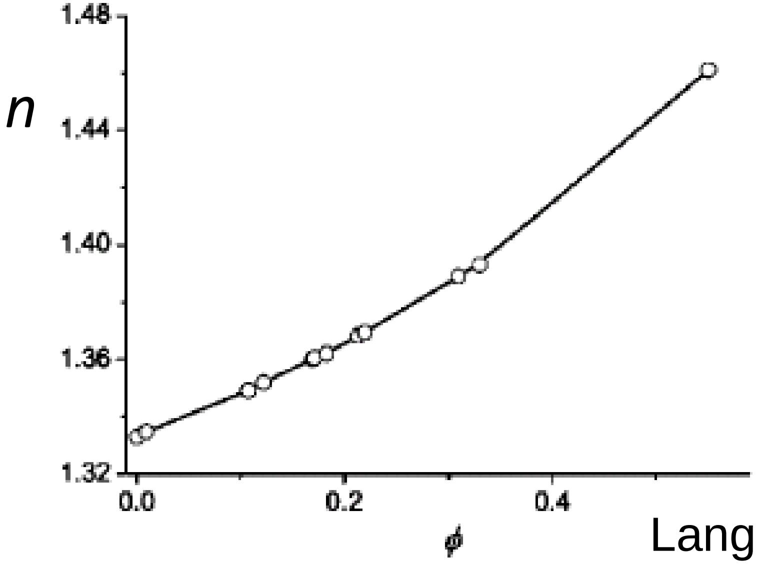
$$\frac{n^2-1}{n^2+2} = \frac{n_p^2-1}{n_p^2+2}\phi + \frac{n_0^2-1}{n_0^2+2}(1-\phi)$$

$$n = n_0 + \phi(n_p - n_0)$$

Refraction index

Particles (p) content in suspension

Solvent refraction index



Turbidity

$$\tau = \frac{4}{9}\pi^4\sigma^3\frac{(n^2-n_0^2)^2}{\phi\lambda^4}$$

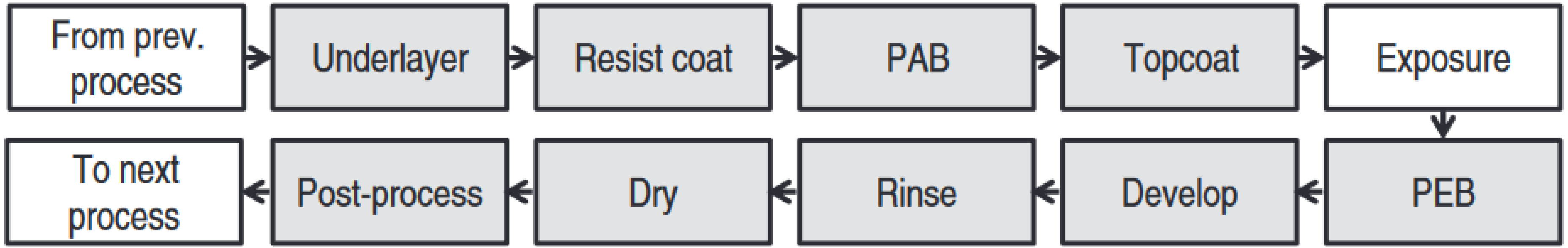
Langmuir 25 (2009) 2390

Resolution:

- line width roughness
- line edge roughness

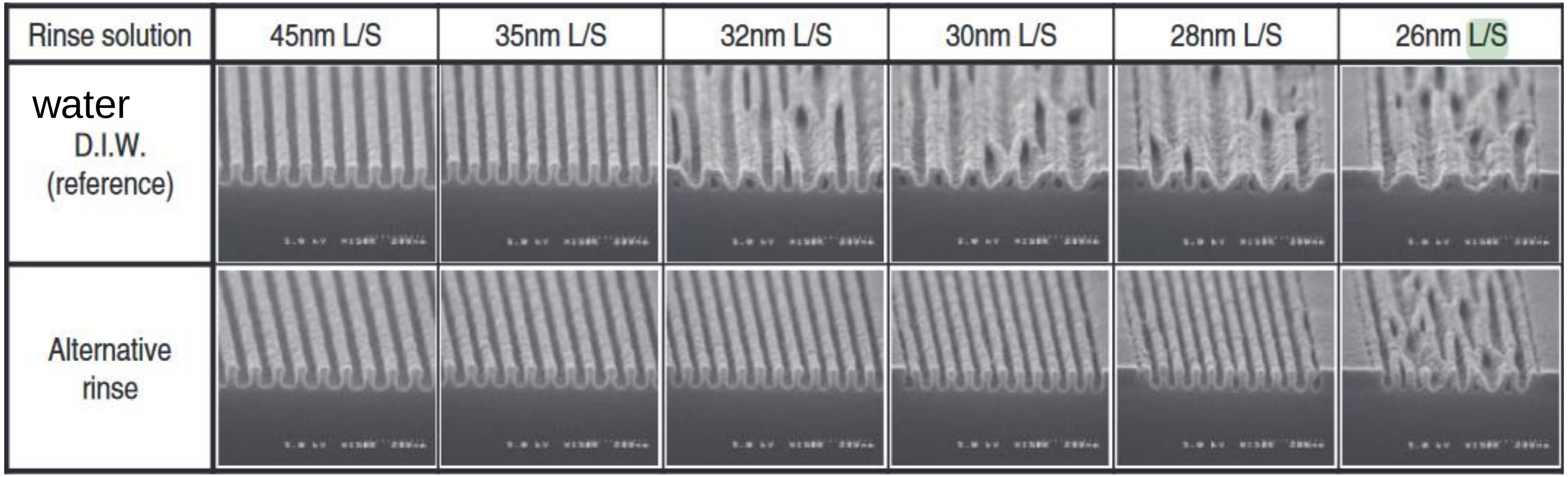
Extreme ultraviolet lithography (EUVL)

Jap. J. Appl. Phys. 52(2013) 010002

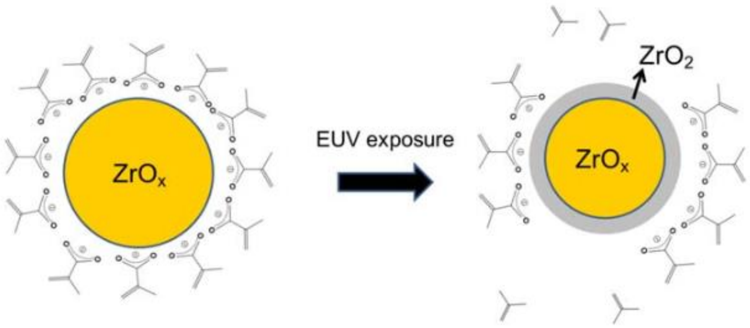


PEB = post-exposure bake

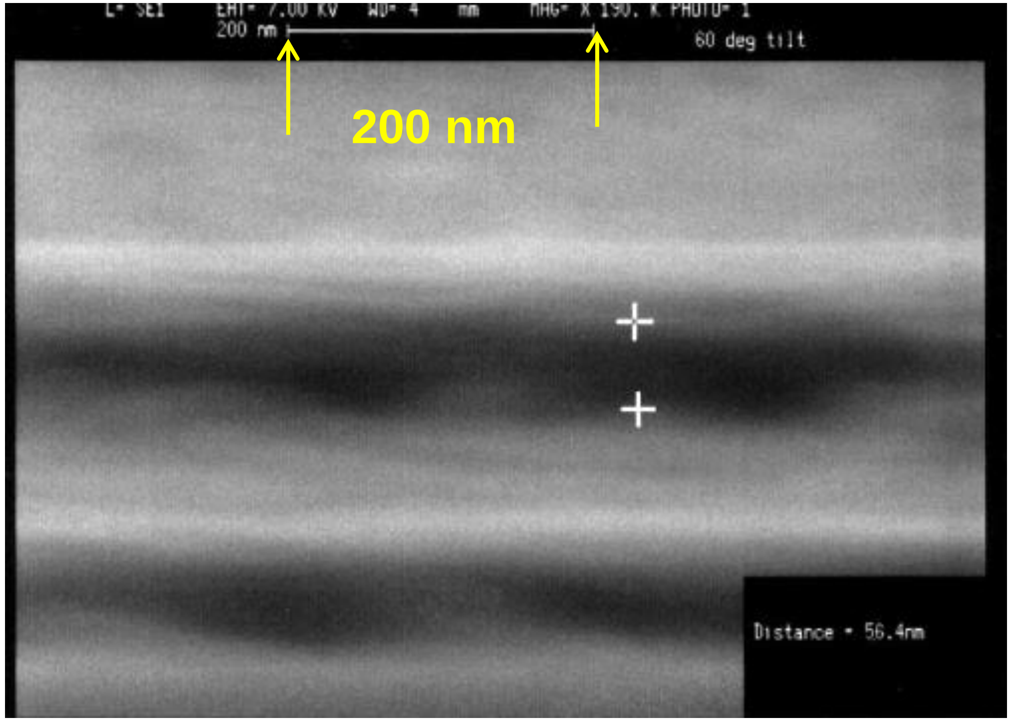
Wetting problem



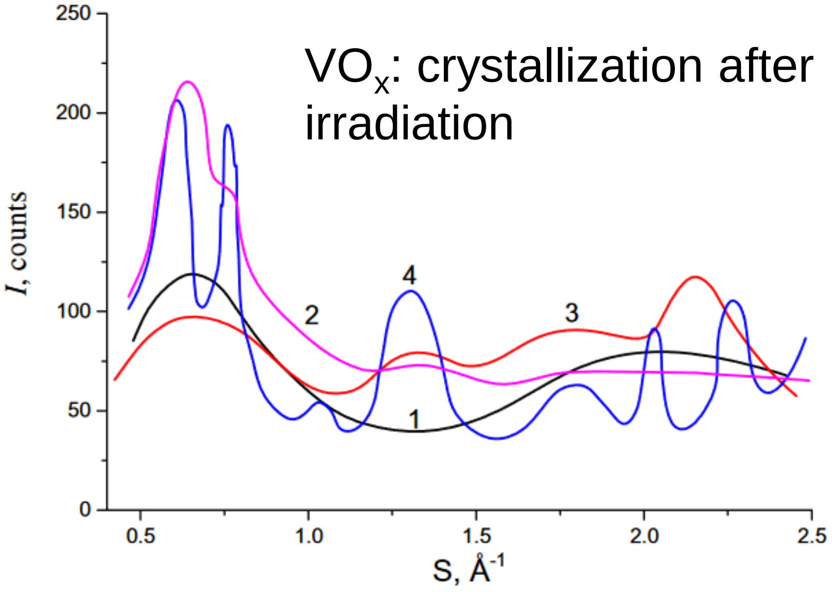
Inorganic resists with increased sensitivity

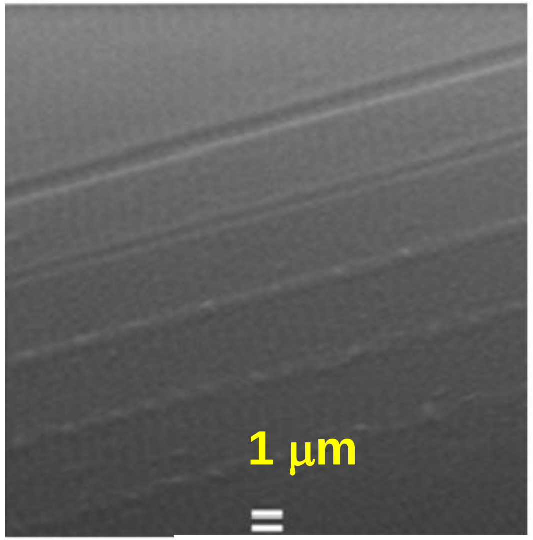


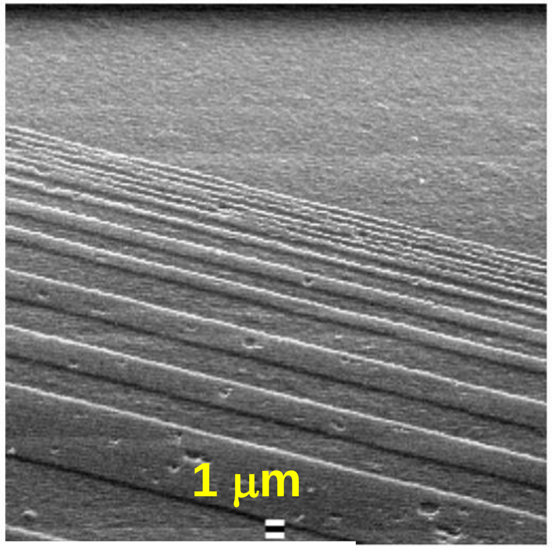
Jap. J. Appl. Physics 58 (2019) SDDC01
(optical lithography)



VO_x: crystallization after irradiation



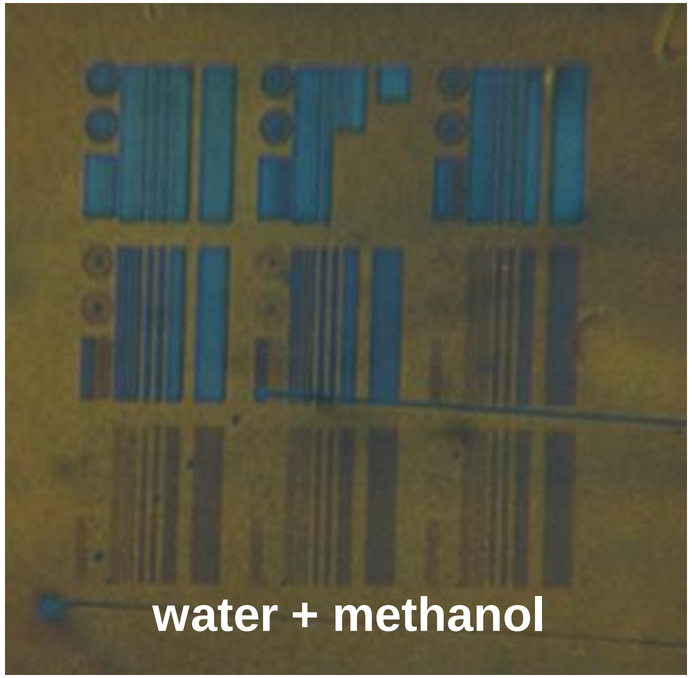




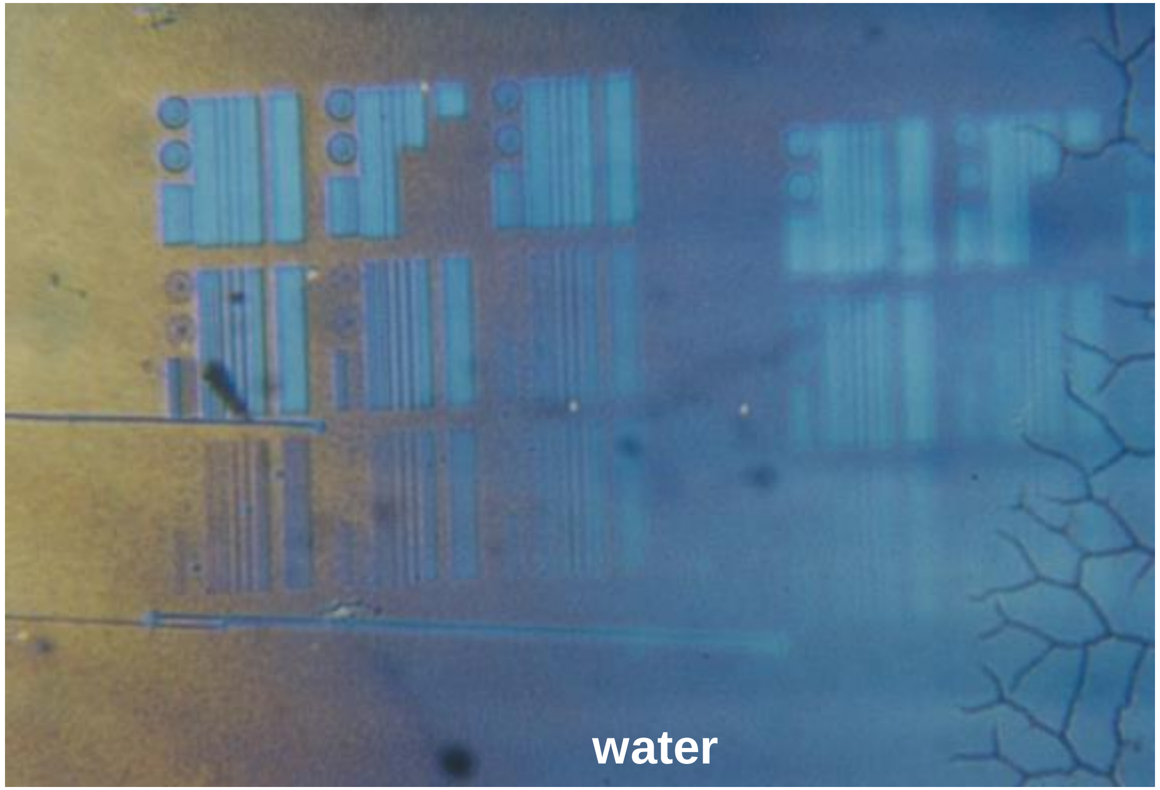
Surface Review and Letters, (2018) 1850118
(e-beam lithography)

Inorganic water-soluble resist: non-stoichiometric vanadium oxide

Dose



Dose

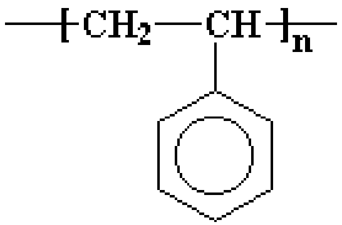


Surface Review and Letters, (2018) 1850118

Composition	Selectivity	Uniformity	Etching rate control	Rate of low oxide etching
Water	High	Low	Temperature	High
Methanol/water	Low	High	Water concentration	Moderate
Formic acid	Moderate	High	Temperature	High
Ethanol/$HClO_4$	High	High	$HClO_4$ concentration	Moderate
Water/potassium hydrogen phthalate		High	Salt concentration	Low

Block-copolymers (maskless process):

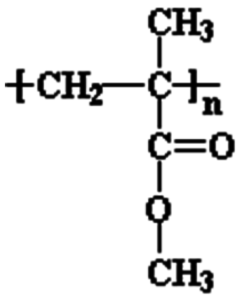
selective etching of certain type of blocks



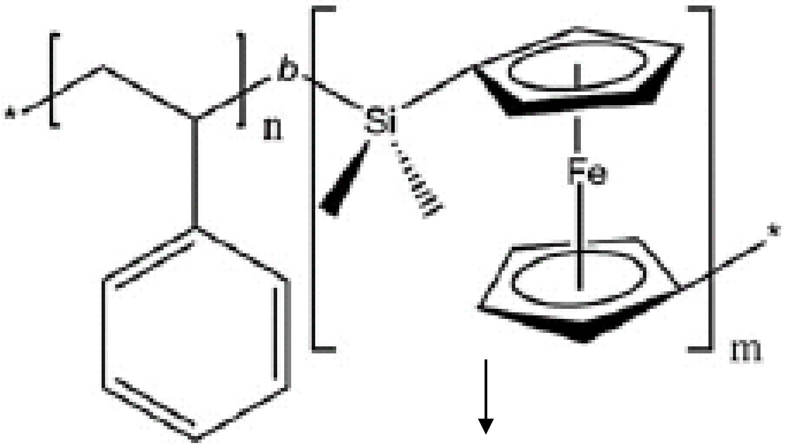
polystyrene

PS-b-PMMA: poly(styrene-block-methyl metacrylate)

(PS и PMMA etching rates in oxygen plasma 1.5:1)

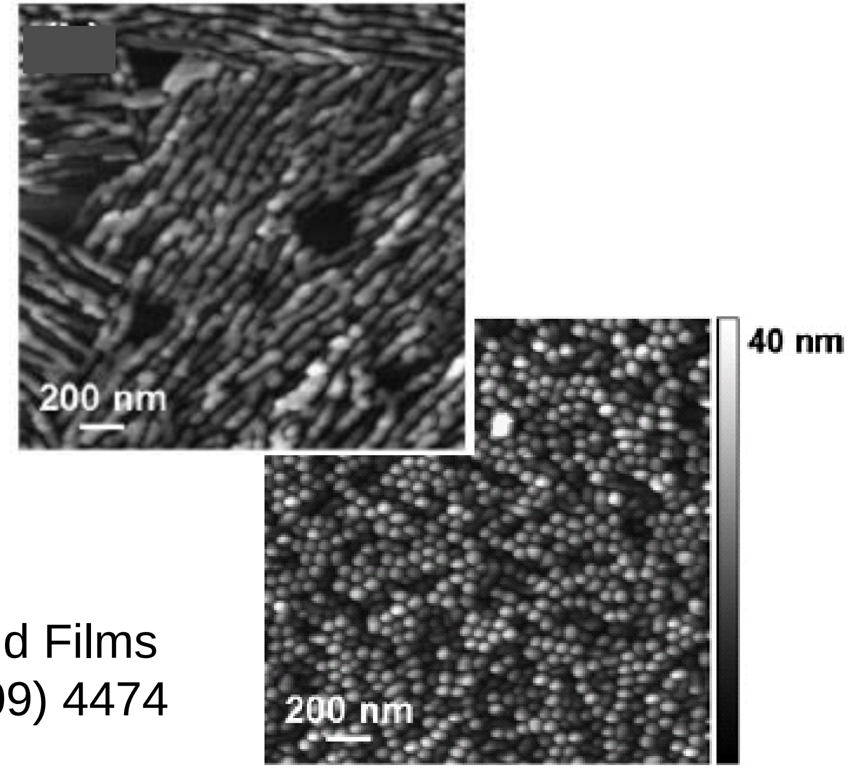


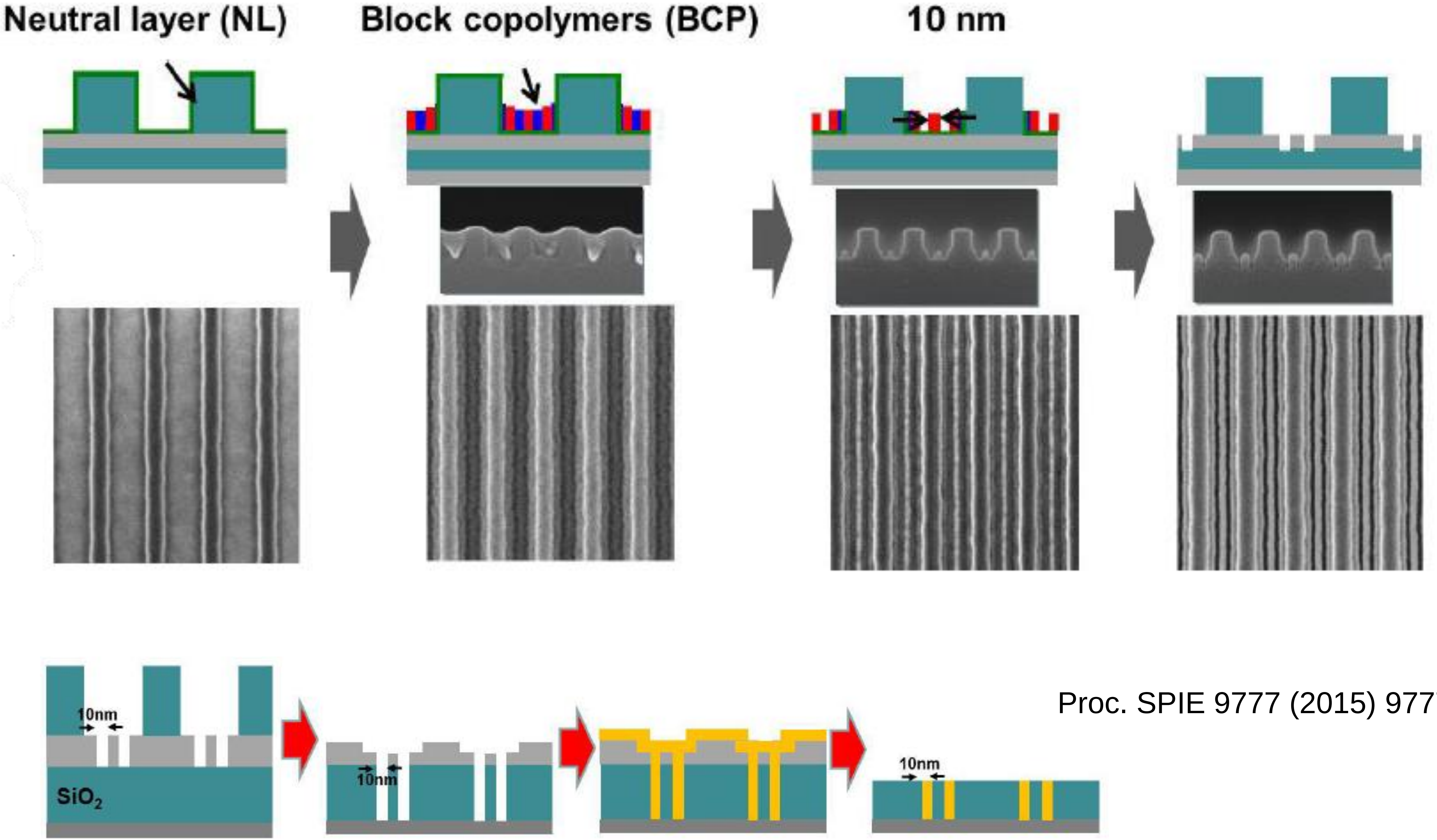
PS-b-PFS: poly (styrene-block-ferrocenyl silane



(Si,Fe)-oxide

Thin Solid Films
517 (2009) 4474





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