High aspect ratio micro/nano machining with proton beam writing

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Proposed approach

Develop a resist formulation suitable for

- Formation of thick films
- High resolution structures
- High Aspect ratio
- High sensitivity
- Processing compatible with Standard Silicon processes
- Stripping with conventional stripping schemes

Develop a patterning technology suitable for

- Fast prototyping
- Thick polymer film structuring
- High resolution patterning

Presentation Outline

- Conventional HAR Patterning Technologies
  - X-Ray lithography (XR-LIGA)
  - I-line lithograpy (UV-LIGA)
- Proton Beam Writing (PBW)
  - Principle of operation
  - Advantages & disadvantages
  - Typical results
- Typical HAR Resists
  - PMMA
  - SU-8
- TADEP resist
  - Formulation
  - Physicochemical properties
  - Formulation & processing optimization
  - Lithographic results
  - Electroplating
- PBW simulation
  - Simulation of Proton beam – Matter interaction
  - Simulation of the thick polymeric films patterning
- Conclusions

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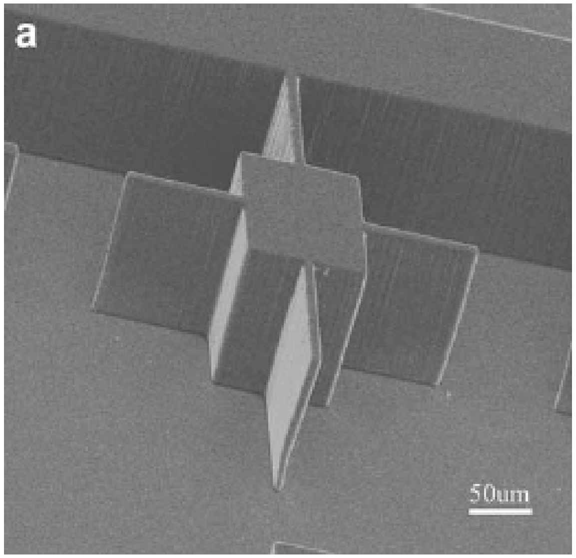
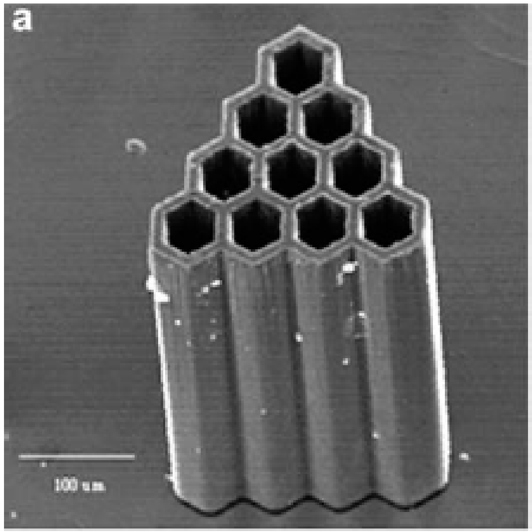
- Conclusions

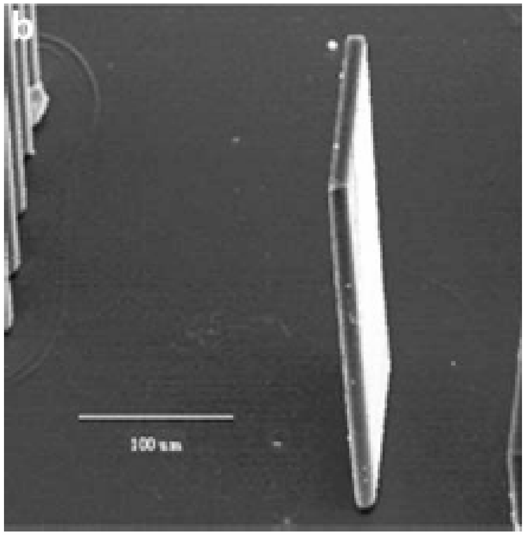
UV-LIGA (typical literature results)



SEM photos of SU-8 microstructure with thickness of 400 μm.
Linewidth: 10 μm

X. Tian, G. Liu, Y. Tian, P. Zhang, X. Zhang
Micros. Techn. 11 265(2005)

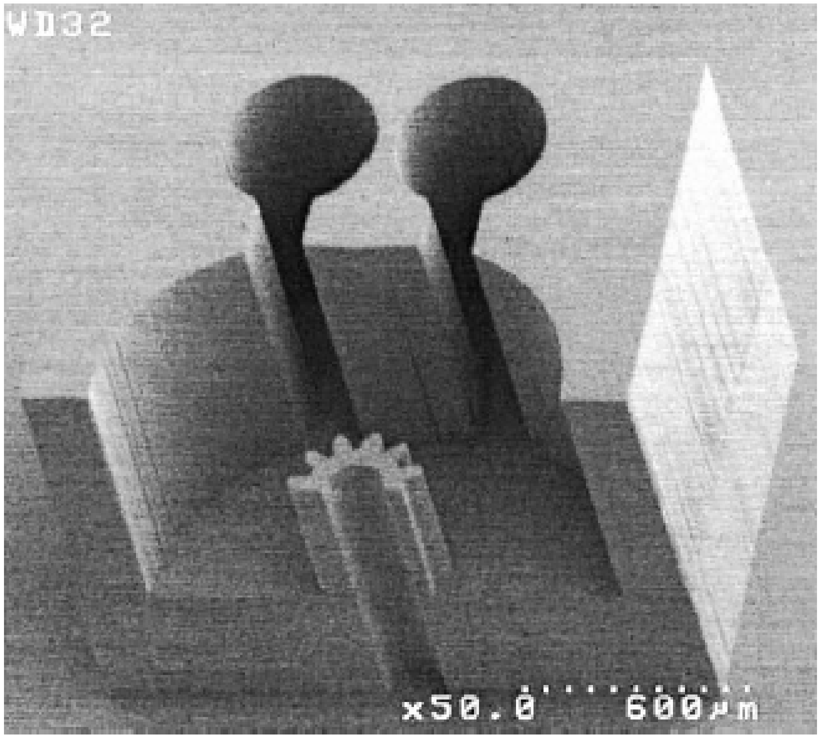




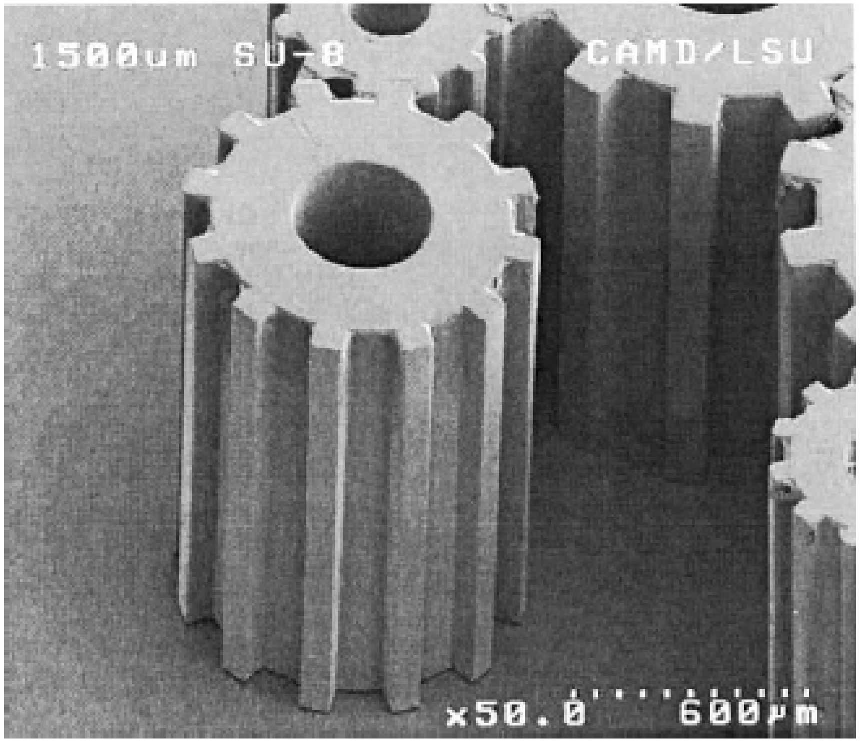
J. Liu, B. Cai, J. Zhu, G. Ding, X. Zhao, C. Yang, D. Chen
Micros. Tech. 10 265(2004)

SU-8 patterns with thickness 210 μm, width 10 μm
Aspect ratio is 21.

X-Ray LIGA (typical literature results)



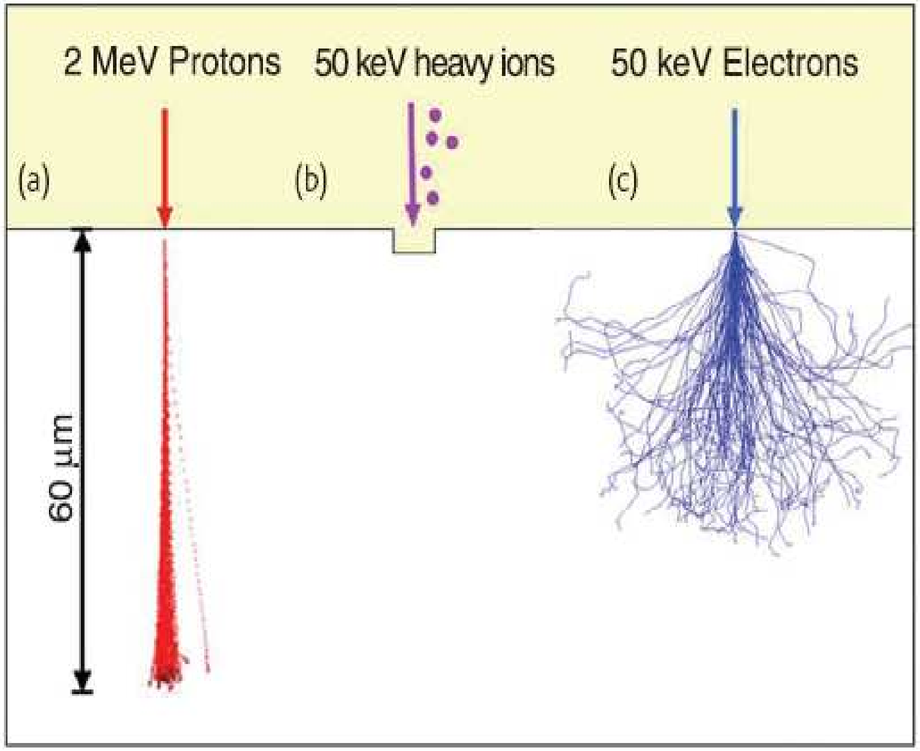
Three-level SU-8 structure with step heights of 300, 600 and 900 μm fabricated by X-ray lithography.



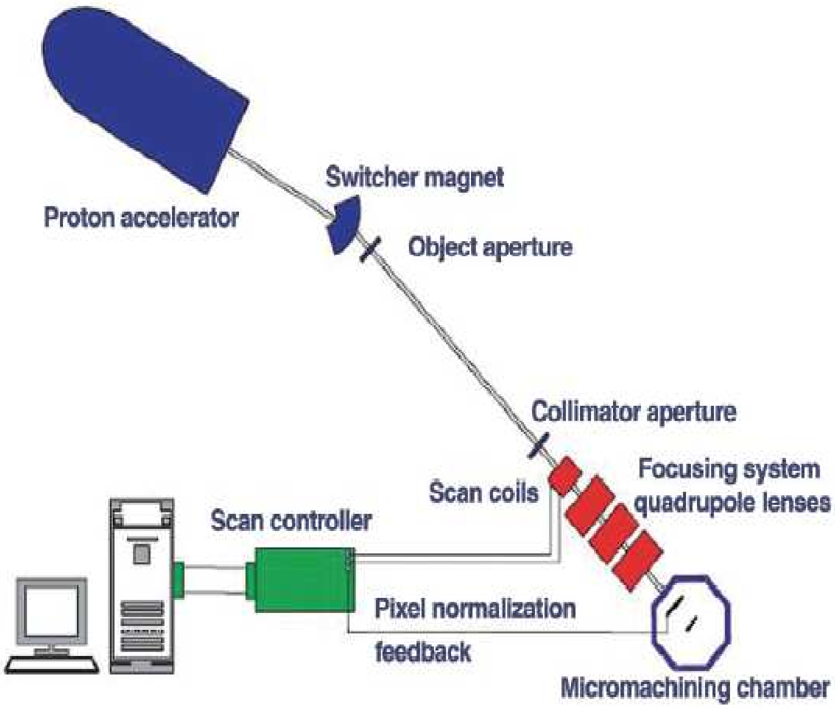
1500 μm tall SU-8 gears.

J. Hormes, J. Göttert, K. Lian, Y. Desta, L. Jian Nucl. Instr. Meth. B 199 332(2003)

Proton Beam Writing (PBW) (I)



Comparison between p-beam writing, FIB, and (c) e-beam writing. The p-beam and e-beam images were simulated using SRIM and CASINO software packages, respectively.



Schematic of the p-beam writing facility at CIBA. MeV protons are produced in a proton accelerator, and a demagnified image of the beam transmitted through an object aperture is focused onto the substrate material (resist) by means of a series of strong focusing magnetic quadrupole lenses. Beam scanning takes place using magnetic or electrostatic deflection before the focusing lenses.

F.Watt, M.B.H.Breese, A.A.Bettiol, J.A.van Kan Materials Today 10(6) 20(2007)

Proton Beam Writing (PBW) (II)

Typical Application areas

- Photonics (waveguides, lens arrays, gratings, …)
- Microfluidic devices, biostructures, and biochips (imprinting, …)
- High resolution patterning (X-ray masks, …)
- Porous Si (patterning, Distributed Bragg reflectors, …)

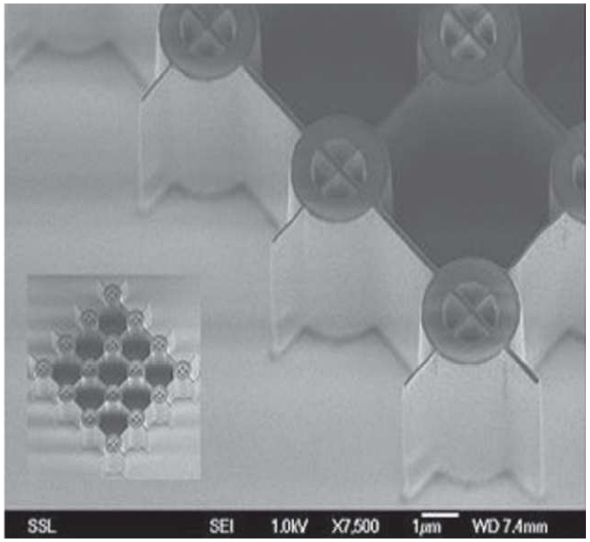
Advantages

- Maskless process (ideal for prototyping)
- Vertical side walls
- Ultra high resolution
- Ultra high aspect ratio pattering (provided the resist properties)

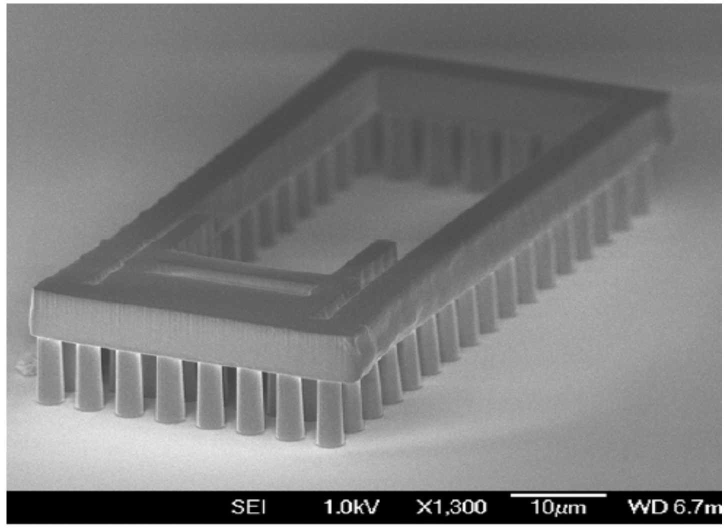
Disadvantages

- Serial patterning process (moderate speed)
- Limited penetration depth (50μm for 2MeV proton beam)

Proton Beam Writing (PBW) (III)

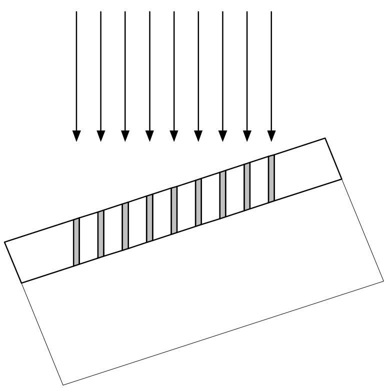


High aspect ratio test structures in SU-8 (60 nm wide, 10µm deep structures).

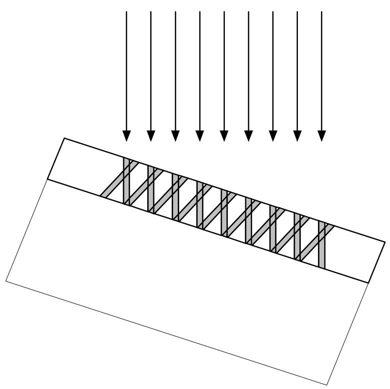


Parthenon's copy with a reduction of 1 million times

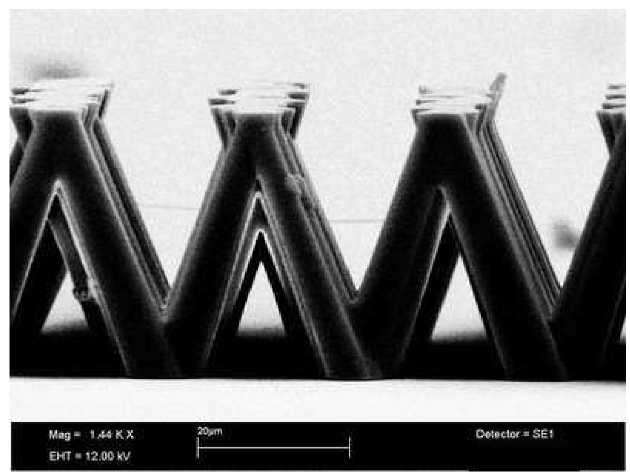
J. A. van Kan, P. G. Shao, K. Ansari, A. A. Bettiol, T. Osipowicz, F. Watt, Microsyst Technol 13 431(2007)



First exposure



Second exposure



Side view of the "lambda" structures.

I.Rajta, M.Chatzichristidi, E.Baradács, I.Raptis, Nucl. Instrum. Meth. B 260 414(2007)

Typical resists for HAR structures

Positive resists

PMMA
Novolak-diazonaphtoquinone resist platform

Negative resists

epoxy based, chemically amplified SU-8

PMMA (I)

Advantages

High resolution

Stripping with conventional stripping schemes (e.g. acetone)

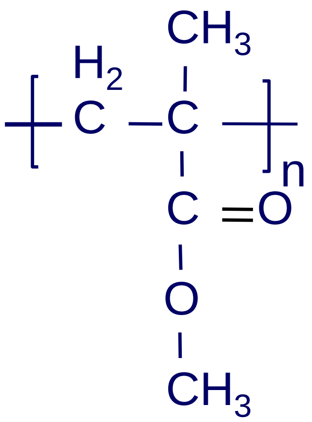
Disadvantages

Limitation in the film thickness obtained by spin coating

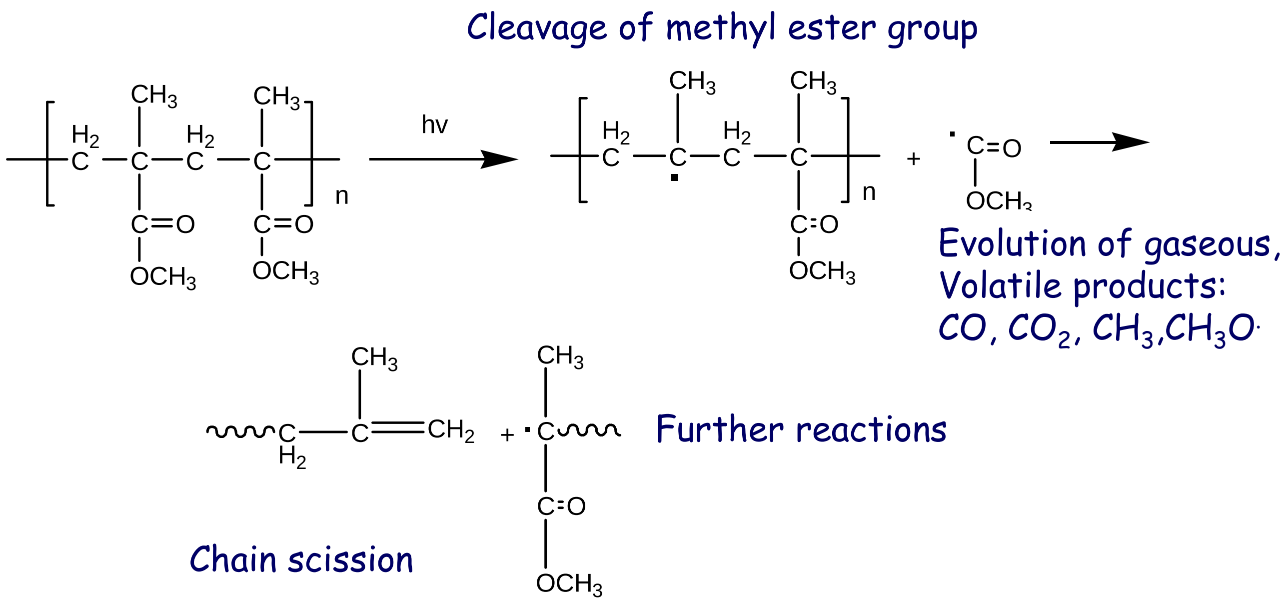
Low sensitivity

Development in organic solvents (MIBK or MIBK/IPA)

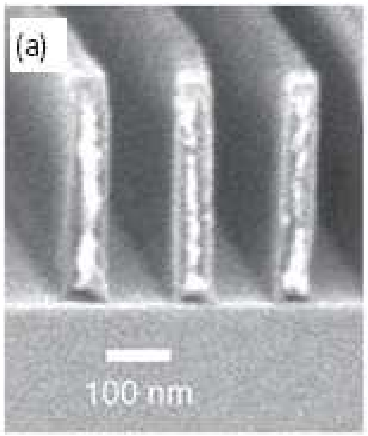
PMMA (II)



PMMA

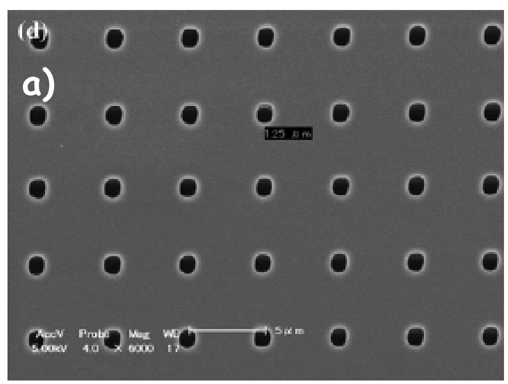


Chain scission mechanism upon exposure



PMMA thickness: 350 nm.
Proton beam: 2MeV
Structure's width: 50nm

F. Watt, M.B.H. Breese, A.A. Bettiol, J.A. van Kan Materials Today 10(6) 20(2007)



SEM image of 5-μm thick PMMA by PBW at 1.7 MeV (fluence: 100 nC/mm^2) with writing patterns of dots (1.25μm diameter).

N. Uchiya, T. Harada, M. Murai,H. Nishikawa, J. Haga, T. Sato, Y. Ishii, T. Kamiya, Nucl. Instr. and Meth. in Phys. Res. B 260405(2007)

SU-8 resist (I)

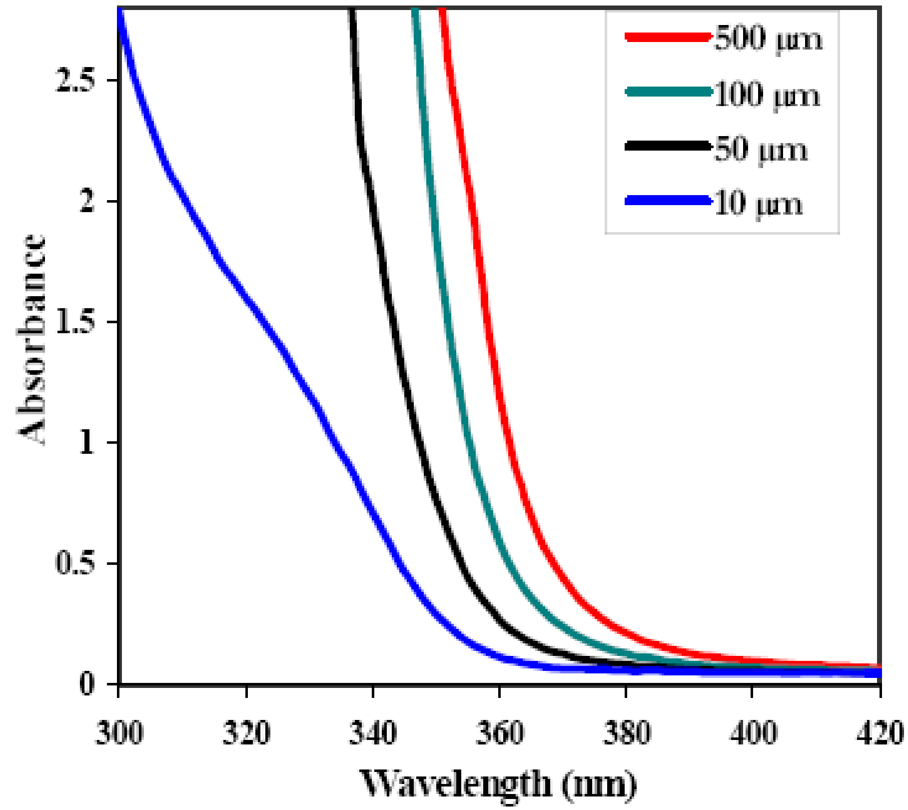
Advantages

- High sensitivity
- Thick films by spin coating

Disadvantages

- Development in organic solvent
- Very difficult stripping by conventional stripping schemes (needs piranha etch, plasma ash e.t.c.)

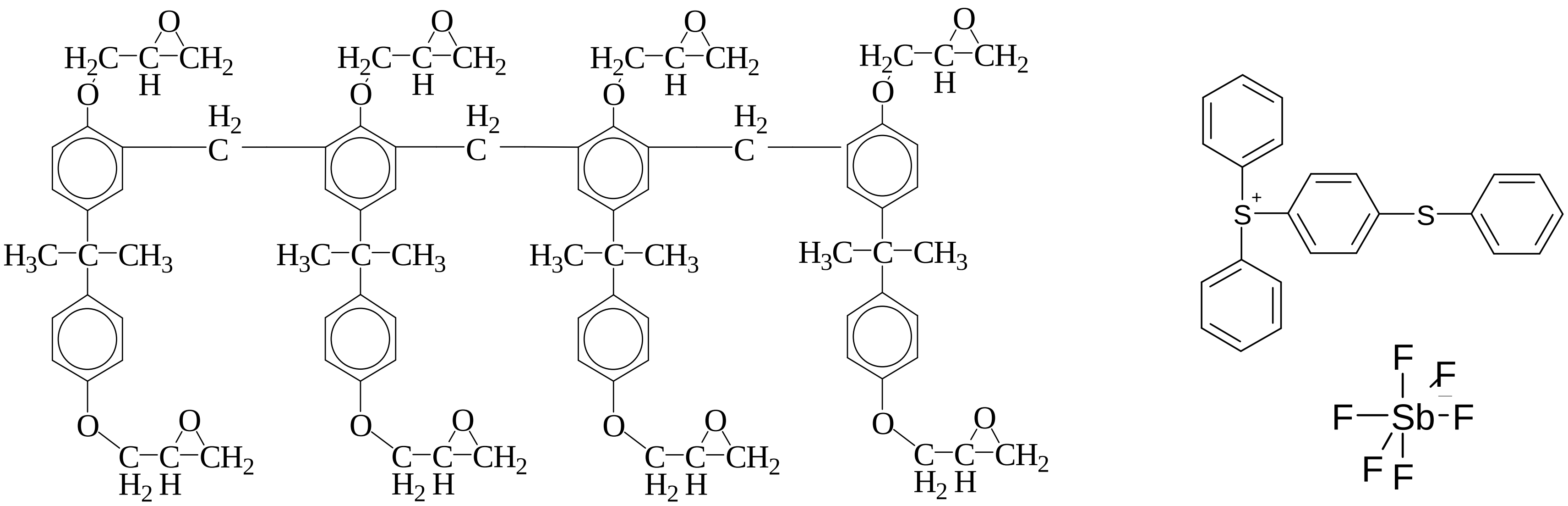
Absorption



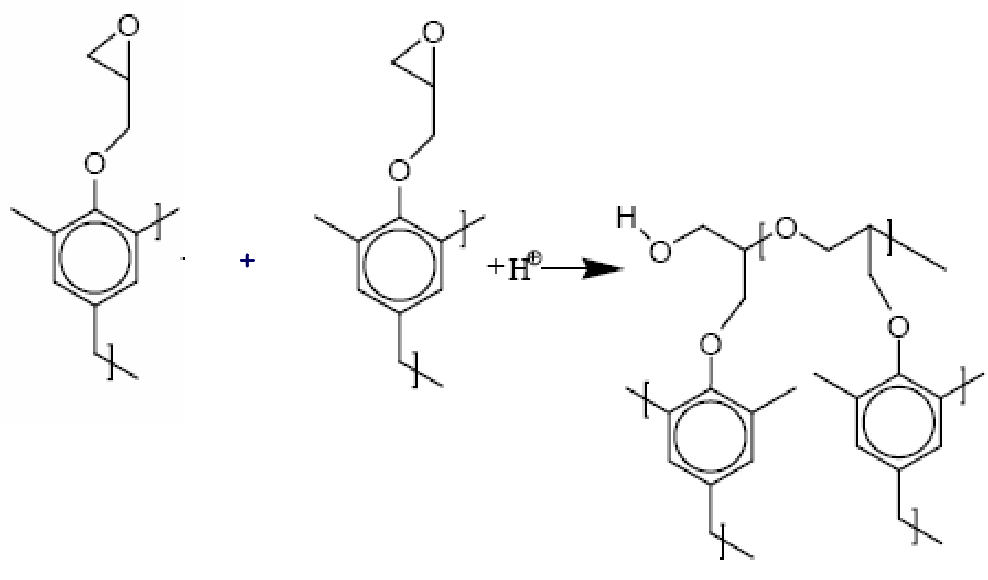
www.microchem.com

SU-8 resist (II)

Chemical formulation of SU-8 resist

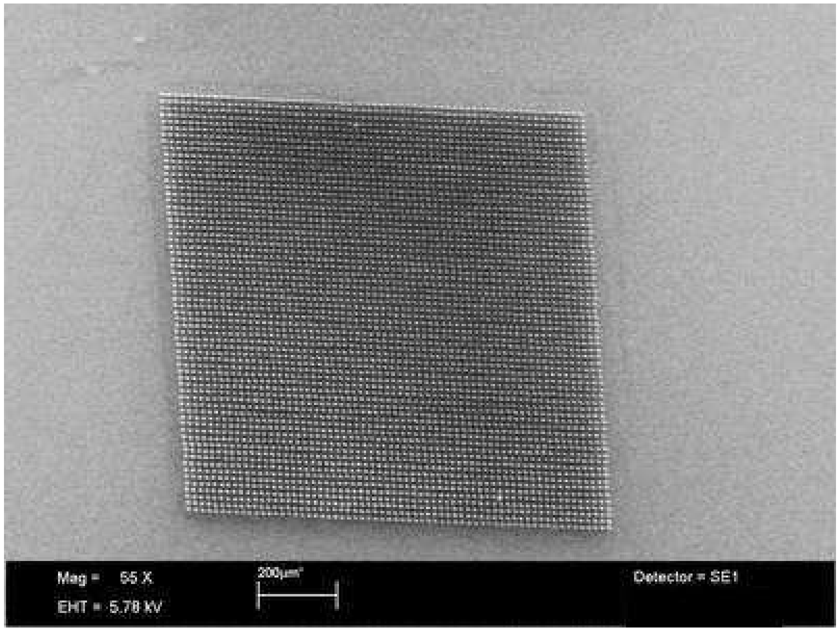


Crosslinking mechanism



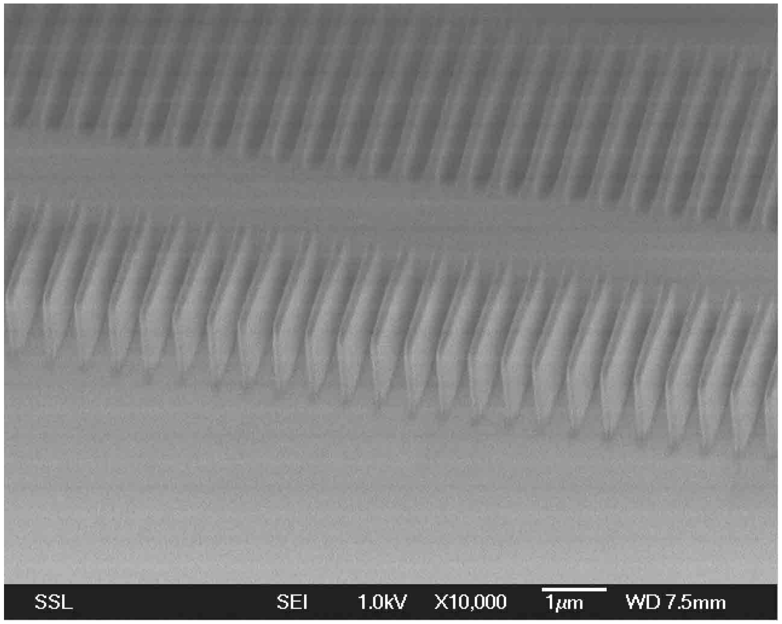
OPEN OF EPOXY RINGS
AND BONDING

SU-8 resist (characteristic PBW results)



1 mm^2 area of single pixel irradiation on SU-8 (top view).

I.Rajta, M.Chatzichristidi, E.Baradács, I.Raptis, Nucl. Instrum. Meth. B 260 414(2007)



Side view of irradiation on SU-8. 130 nm wide lines, 15 aspect ratio

J.A. van Kan, P.G. Shao, K. Ansari, A.A. Bettiol, T. Osipowicz F. Watt, Microsyst. Technol. 13 431(2007)

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TADEP formulation

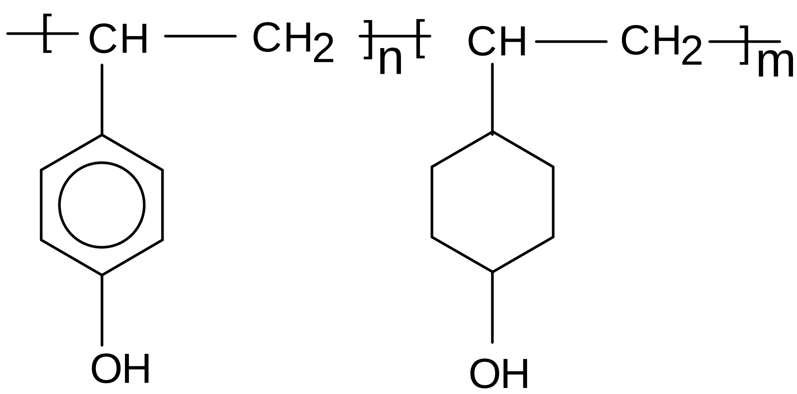
Thick Aqueous Developable EPoxy resist

Goal:

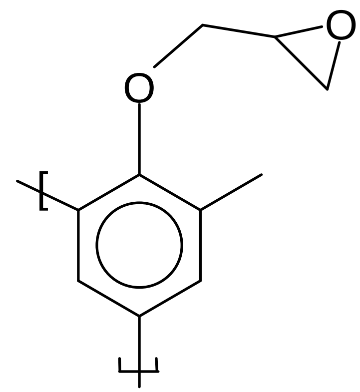
Develop a resist formulation suitable for

- Formation of thick films
- High resolution structures
- High Aspect ratio
- High sensitivity
- Processing compatible with Standard Silicon process
- Stripping with conventional stripping schemes

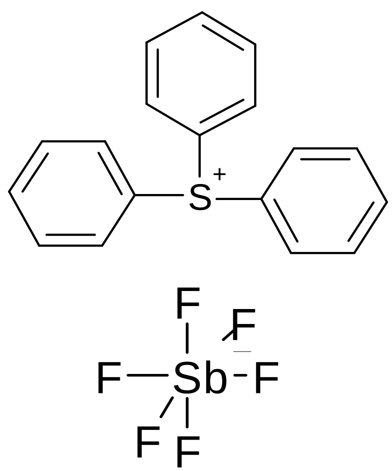
TADEP formulation



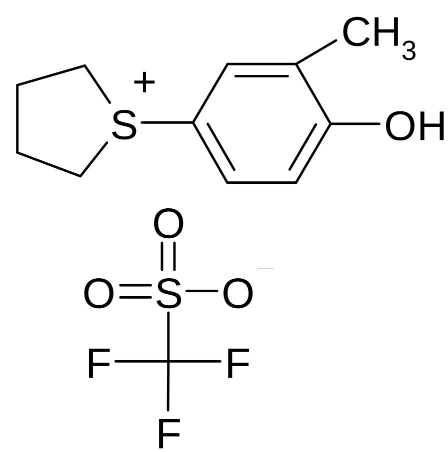
Partially Hydrogenated PHS
from Maruzen Co.



Epoxy novolac
Fractionation of EPICOTE 164 from Shell

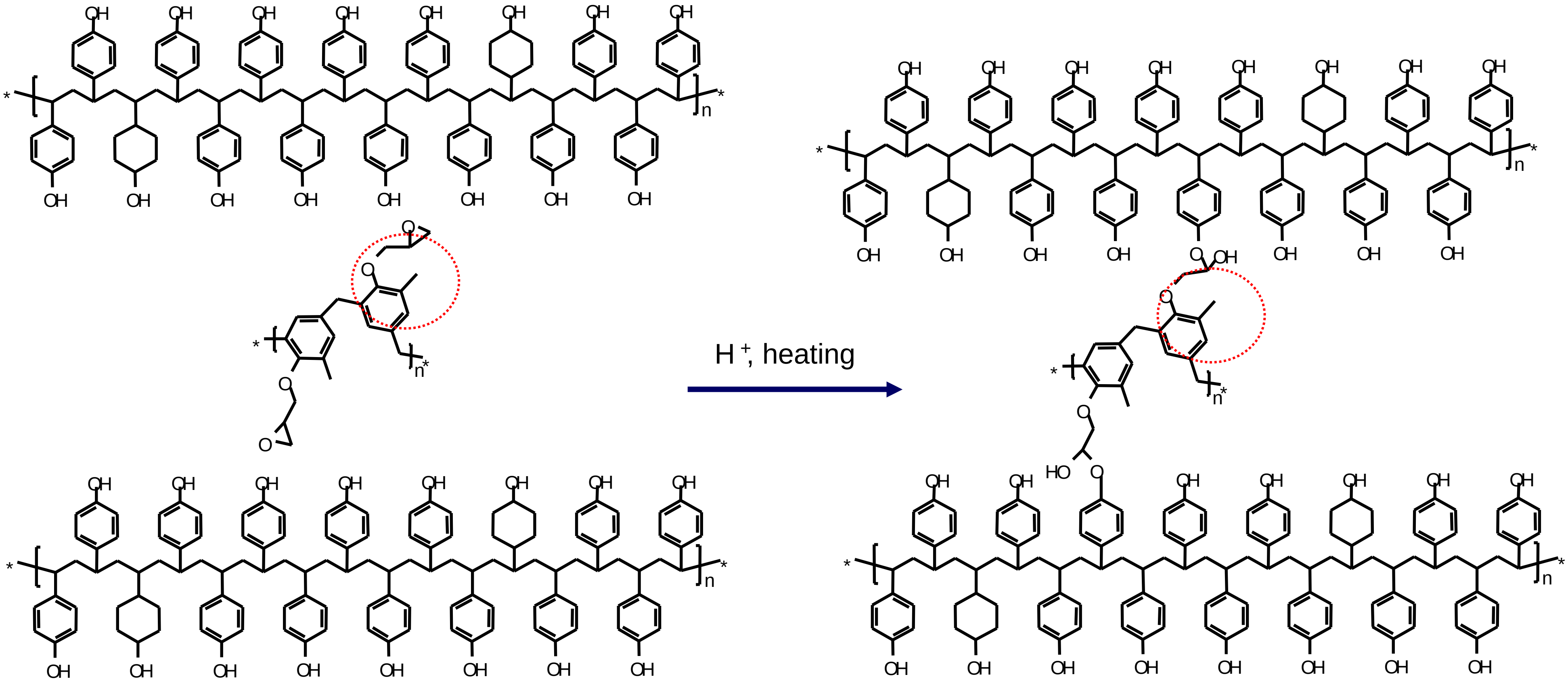


Triphenyl Sulfonium Hexafluoro Antimonate (TPS-SbF_6)



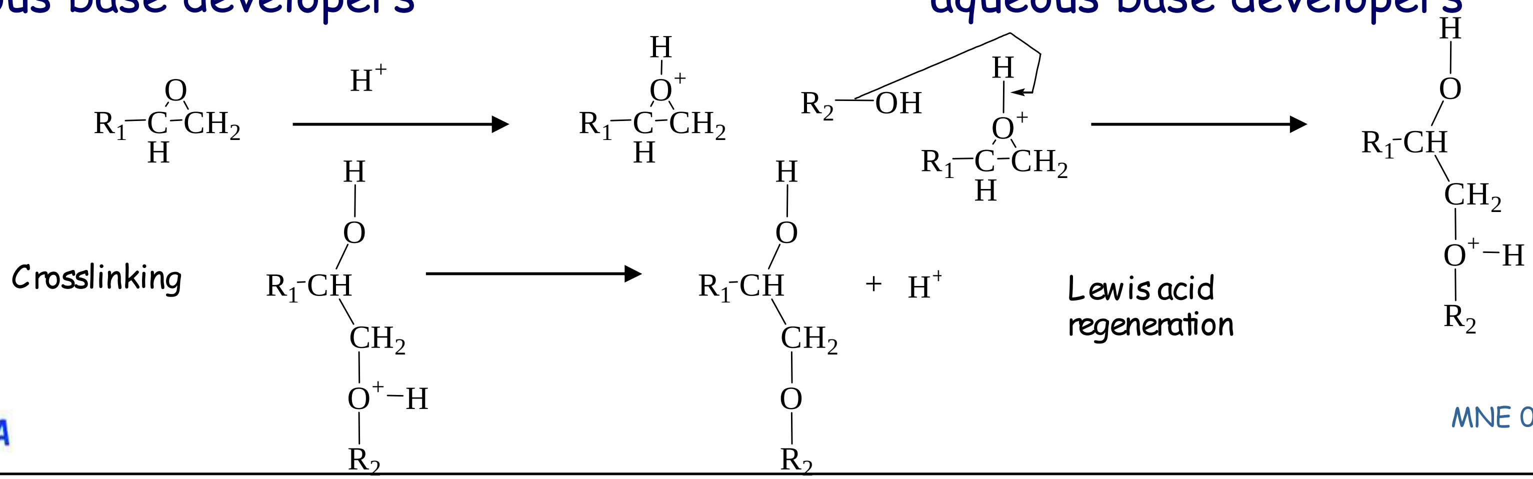
1-(4-hydroxy-3-methylphenyl) tetrahydrothiophenium triflate (o-CS-triflate)

TADEP Crosslinking mechanism



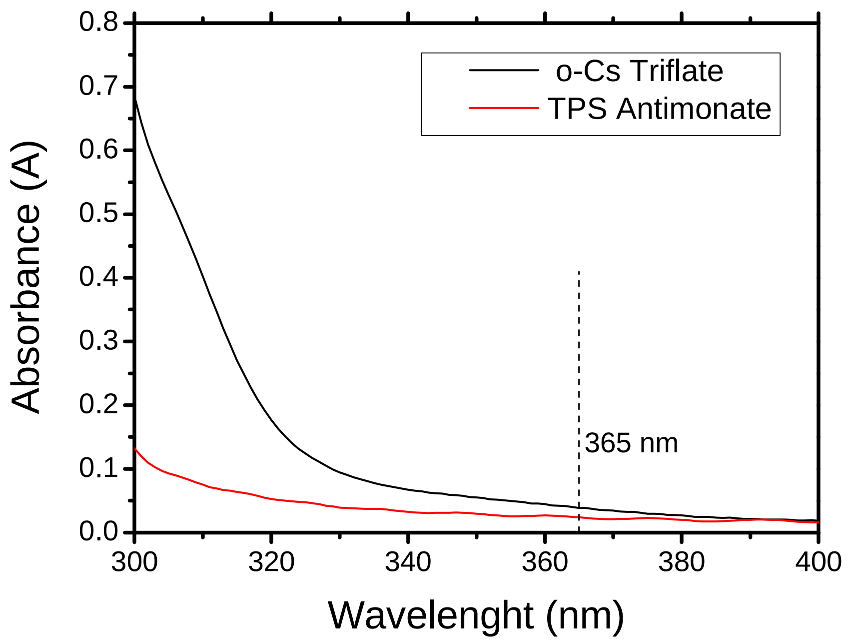
Unexposed Resist Areas: Soluble in aqueous base developers

Exposed Resist Areas: Insoluble in aqueous base developers

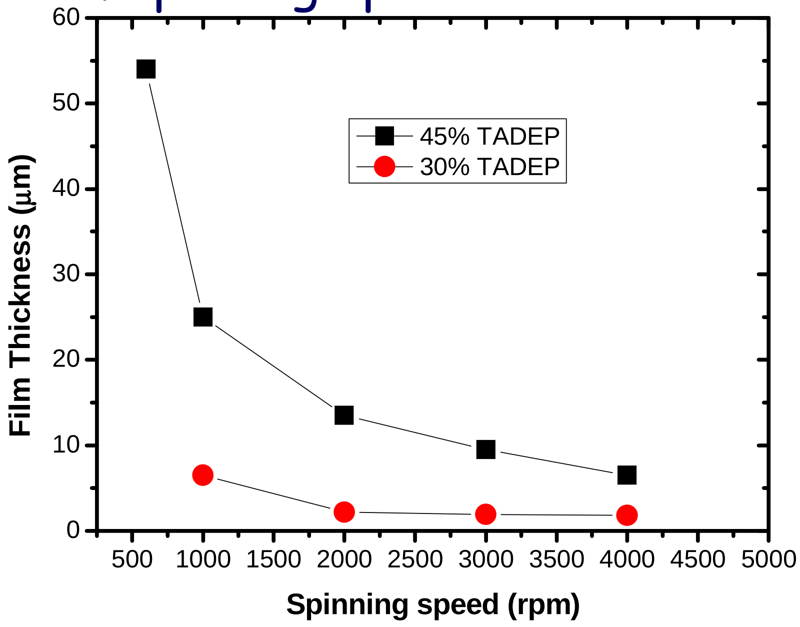


Thickness- Absorption data

PAG's UV spectra



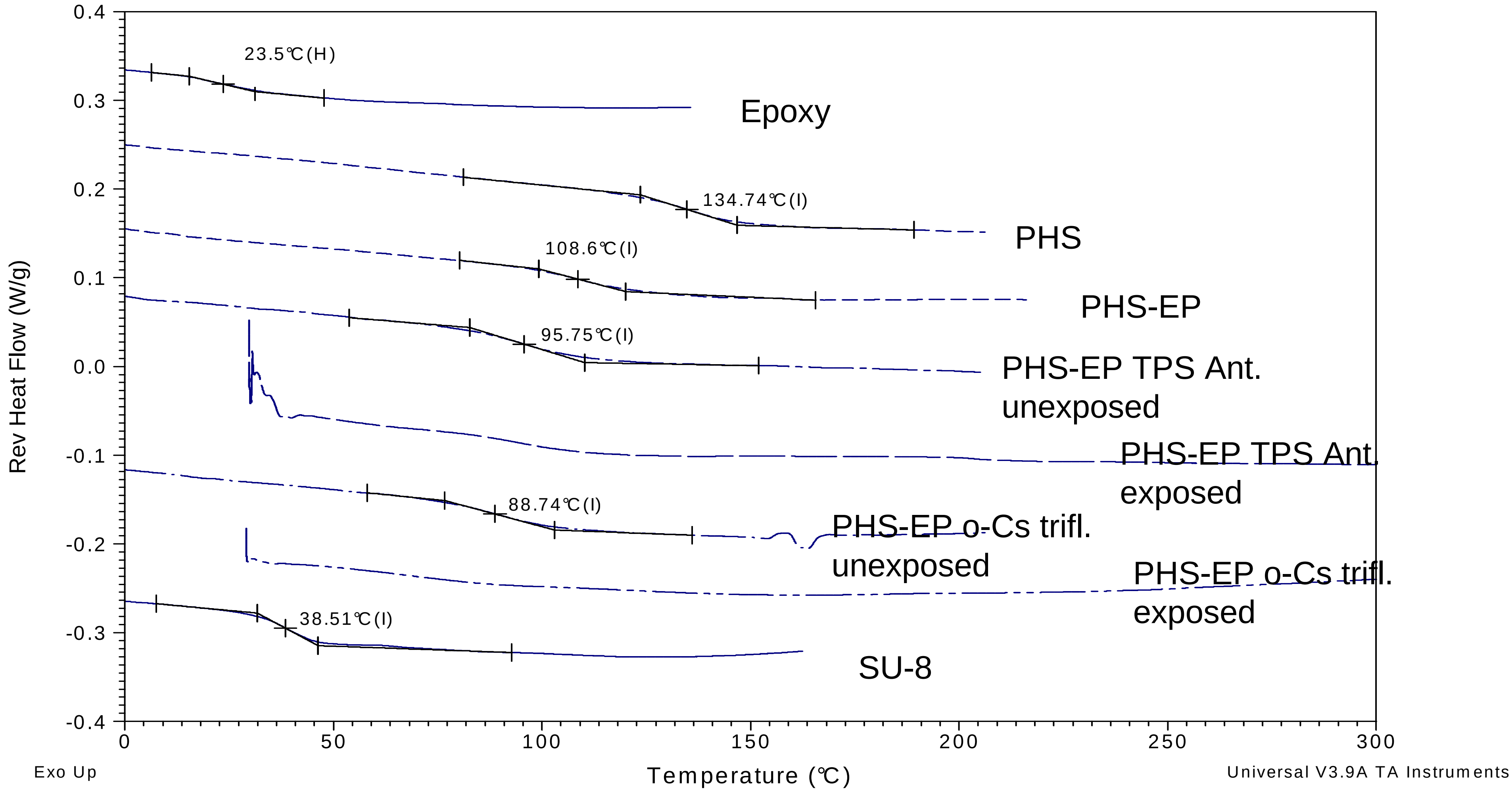
TADEP film thickness (after PAB) vs. spinning speed



It is shown that at 365nm, where the film is exposed, the TPS-antimonate does not absorb whereas o-Cs triflate absorbs slightly.

55μm thick film can be achieved with one spinning

Glass transition temperature studies

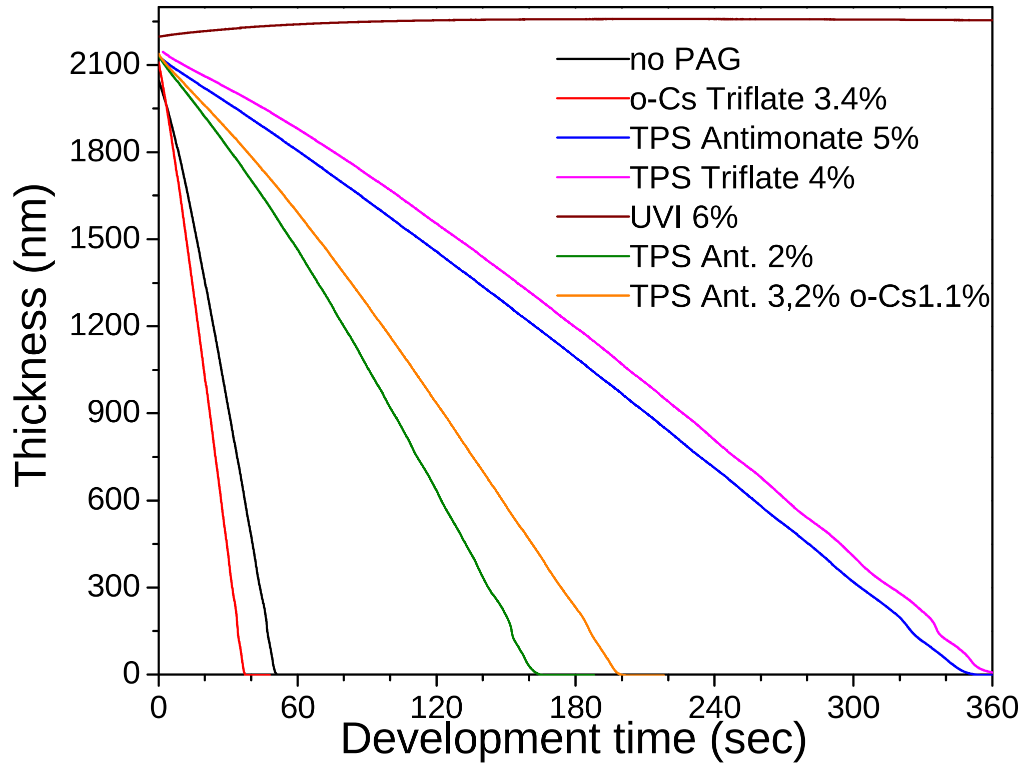


The resist components are fully miscible
The exposed areas are crosslinked and show no Tg

Dissolution study (PAG molecule)

Concept: Controlled development process

Tool: White Light Reflectance Spectroscopy DRM



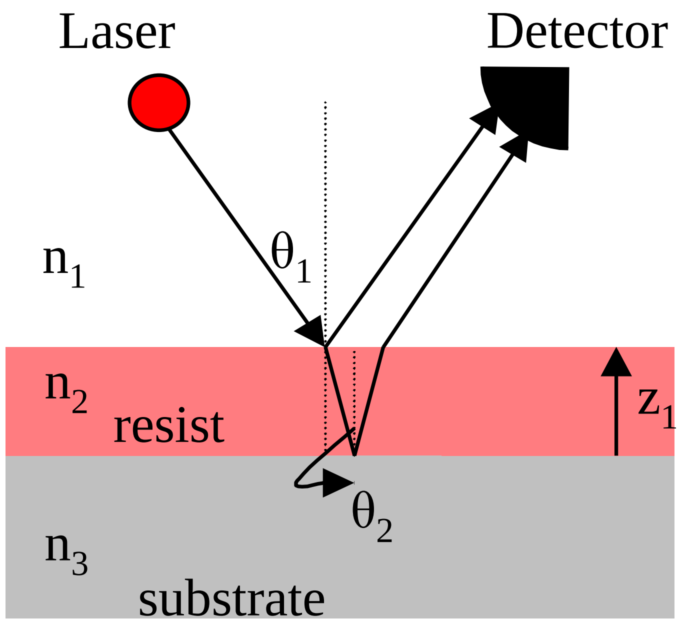
Film thickness: ~2μm

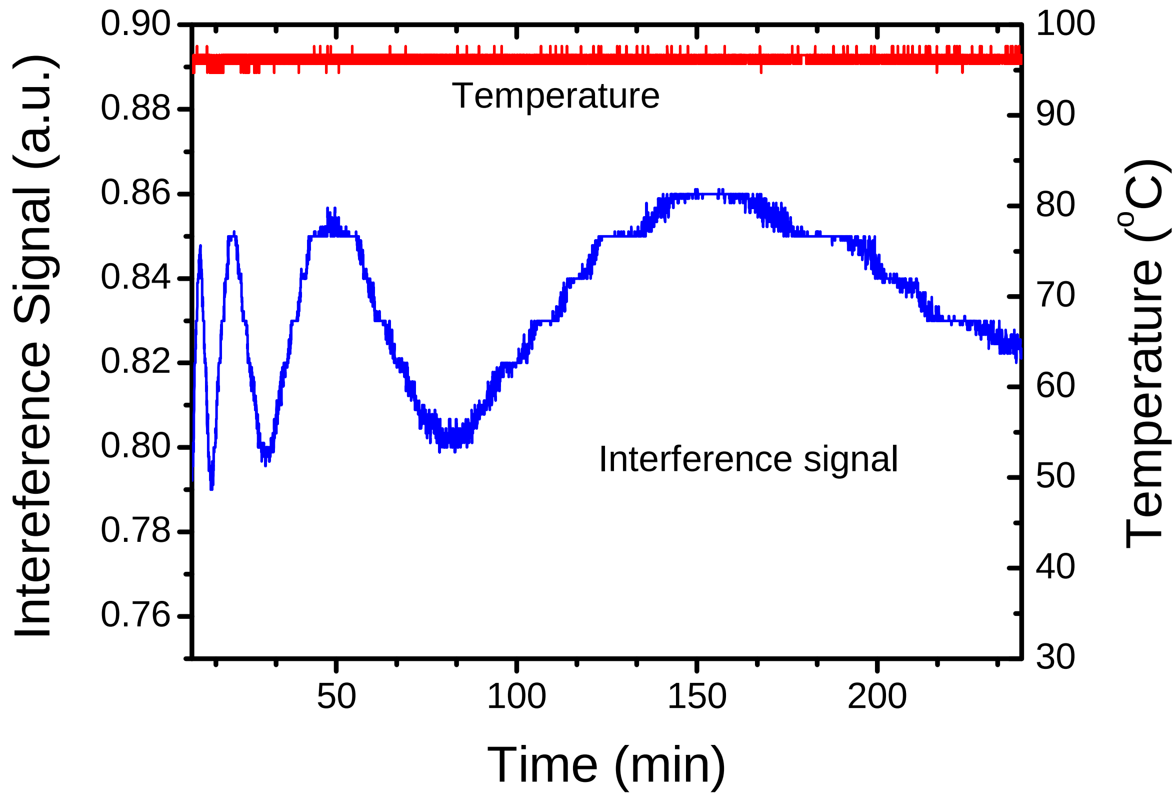
Developer: AZ-726 (AZ-EM) 0.26N TMAH

In all cases dissolution proceeds linearly with time.
NO swelling effect is observed except in the UVI case which is very hydrophobic.
In the SU-8 resist case, the development is abrupt (impossible to monitor).

P-RES-4 "Processing effects on the dissolution properties of thin chemically amplified photoresist films"

PAB study





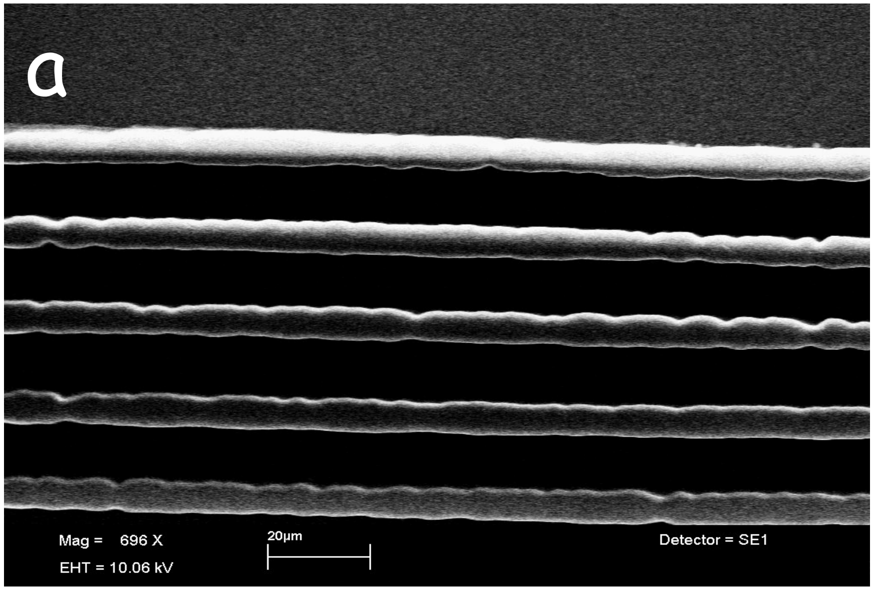
Operating principle

Single Wavelength Interferometer Set-up

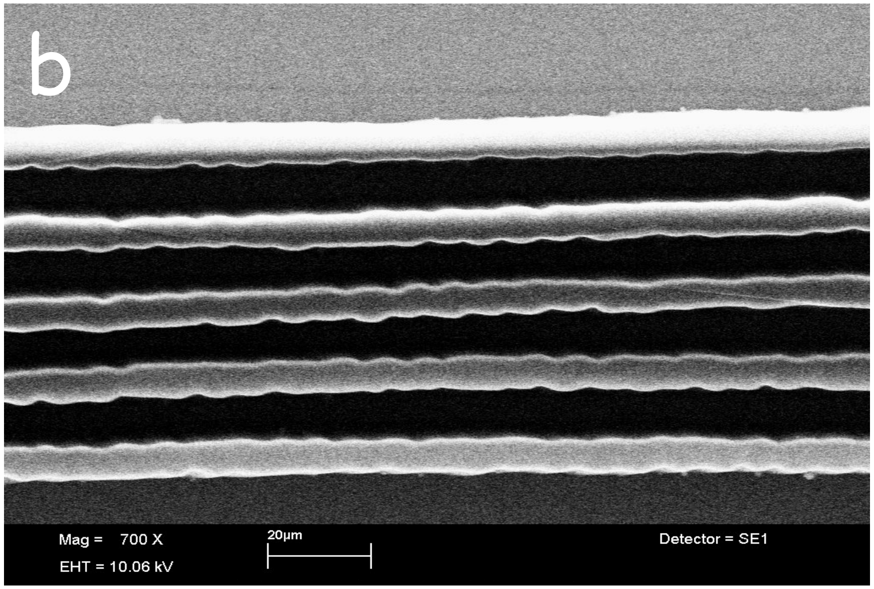
Solvent evaporation during the PAB step. Most of the solvent evaporates during the first 10min (heat up from RT to 95°C). During the rest period (4h) ~0.8μm of resist thinning is observed.

PEB study

100°C for 8 min
exposure dose (238 nC/mm^2)



110°C for 8 min
exposure dose (116 nC/mm^2)



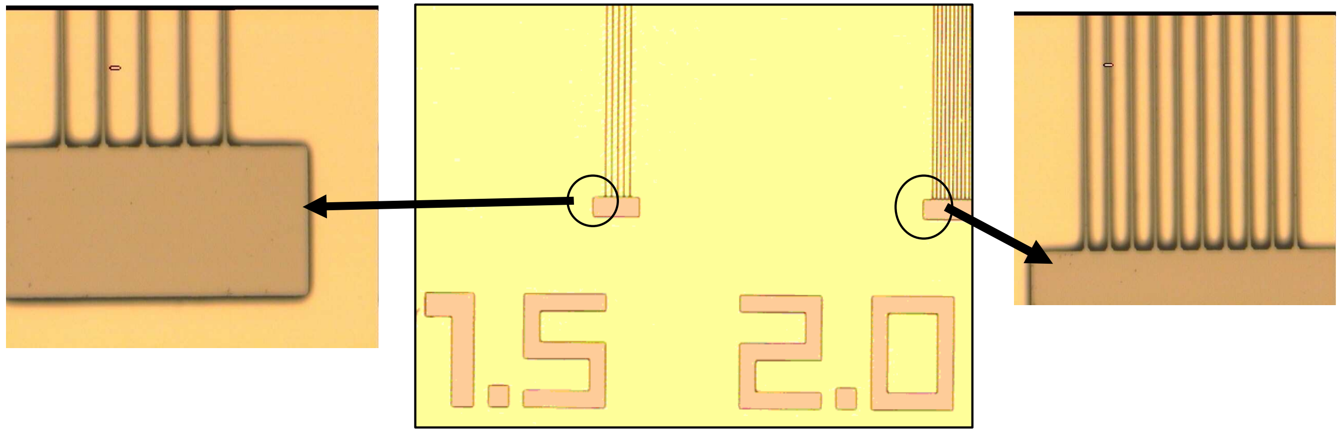
The increased PEB temperature helps significantly the crosslinking reaction

I. Rajta, E. Baradacs, M. Chatzichristidi, E.S. Valamontes, I. Raptis, Nucl. Inst. Meth. B, 231 423 (2005)

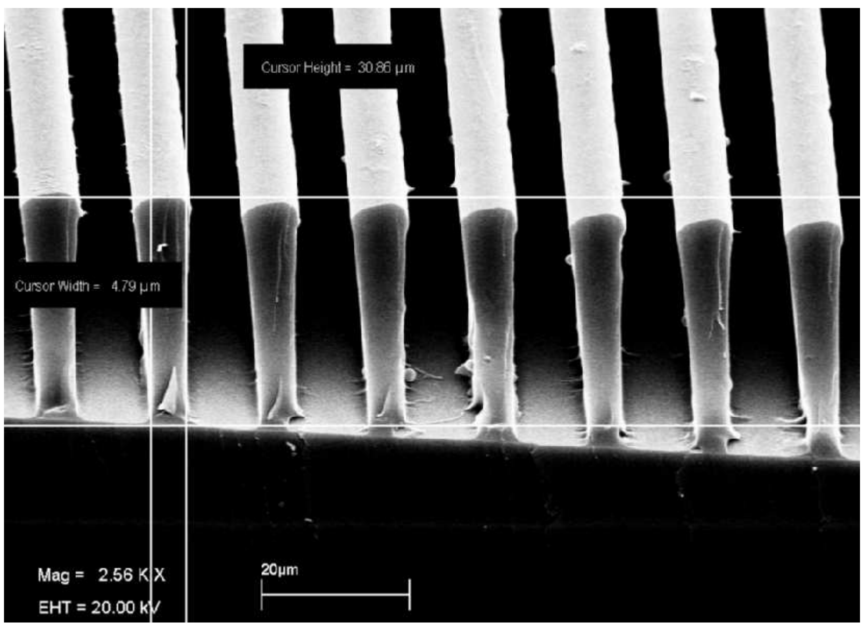
Preliminary Lithographic evaluation (I)

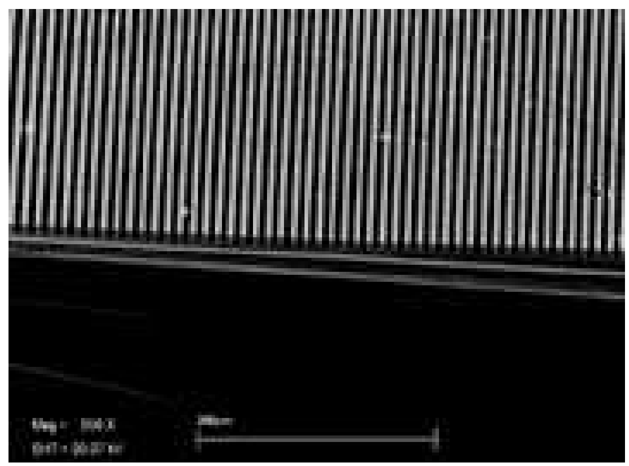
UV-LIGA

Thickness = 11 μm
Aspect Ratio = 7



Substrate: Silicon wafer with plating base (Au surface)





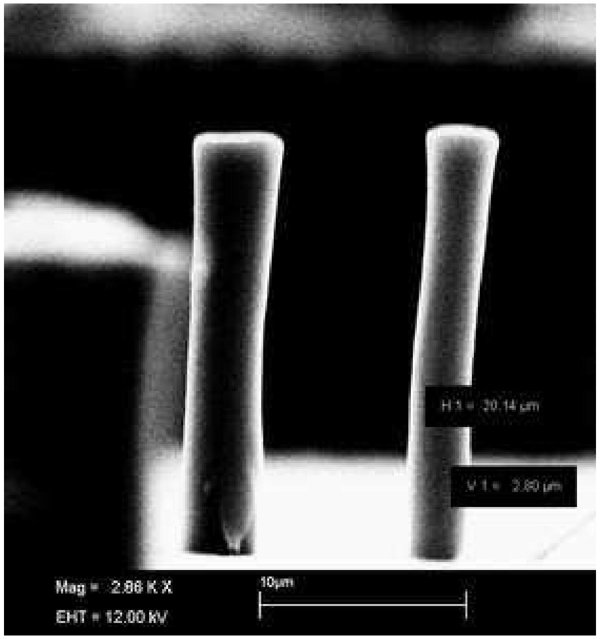
Thickness = 35 μm
Layout = 5 μm L/S
Linewidth = 5 μm

I-line lithography (MJB3 Karl-Suss)

Preliminary Lithographic evaluation (II)

SINGLE PIXEL AND SINGLE LINE EXPOSURES

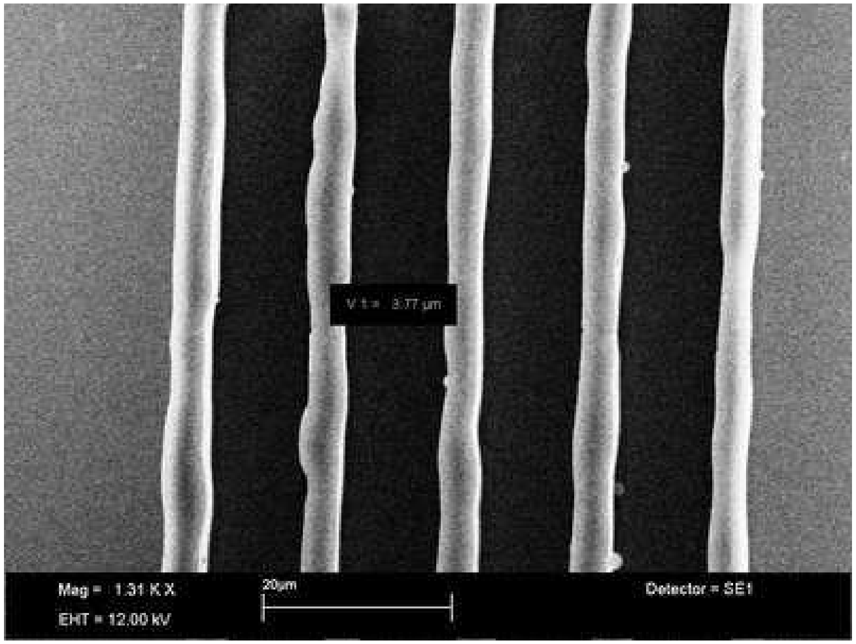
The achieved smallest feature size was the same as the measured beam spot size (limited by the proton beam dimensions). The highest aspect ratio for this type of structures was 7 (for the selected film thickness).



Side view of single pixel irradiation on TADEP.

Resolution 2.8µm

Aspect ratio 7

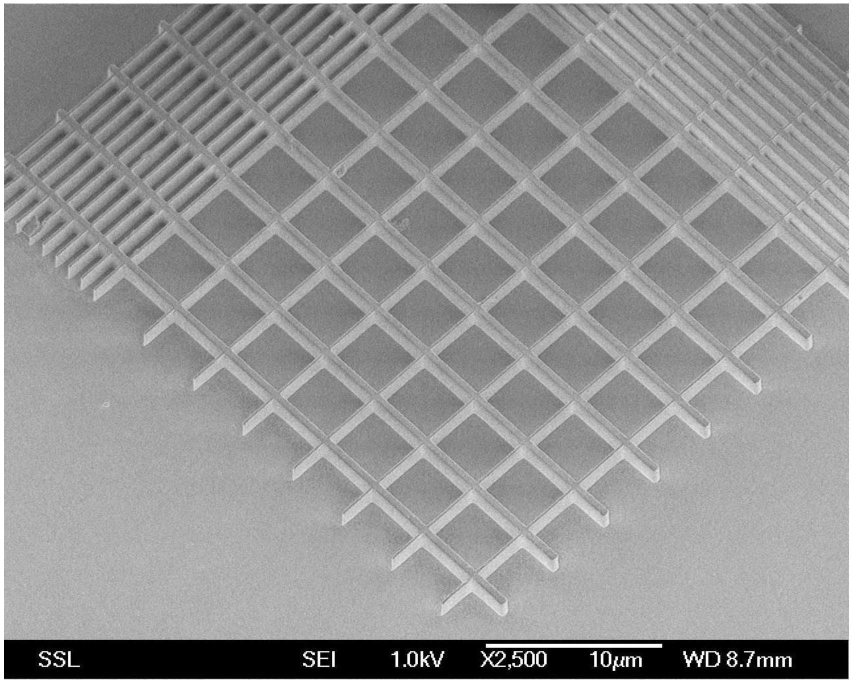


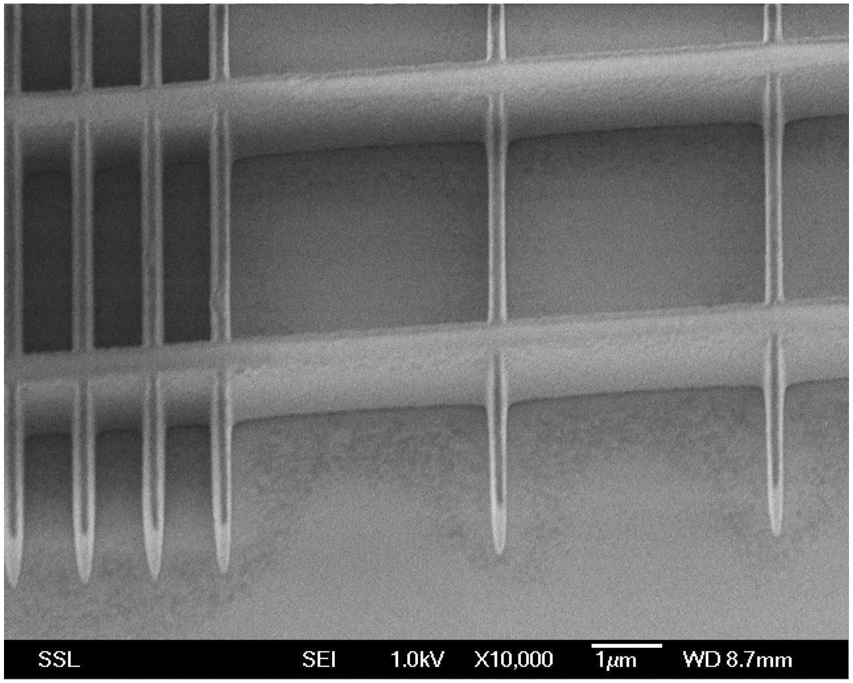
Top view of single line irradiation on TADEP.

Beam size: ~ 3X3µm

I.Rajta, M.Chatzichristidi, E.Baradács, I.Raptis, Nucl. Instrum. Meth. B 260 414(2007)

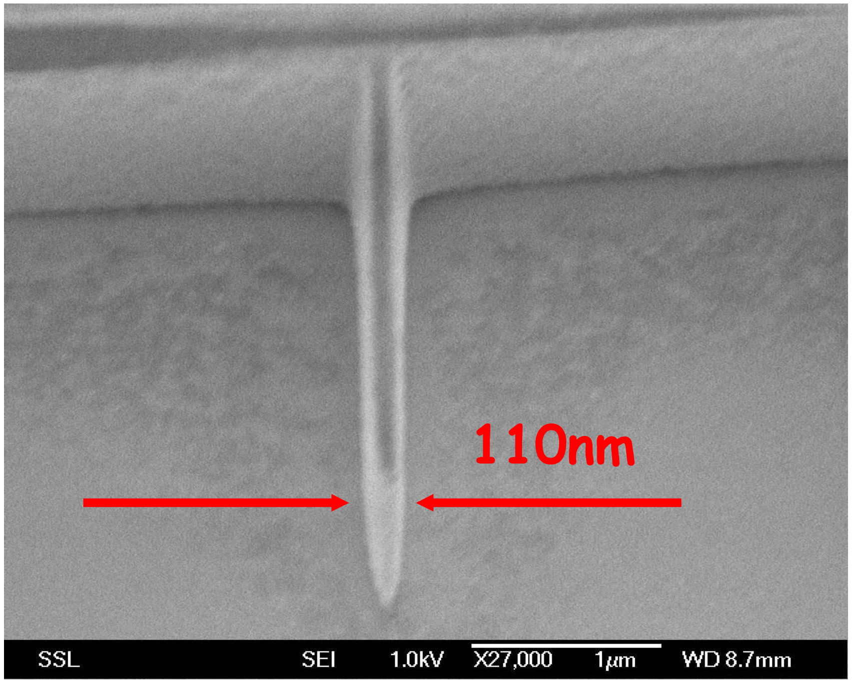
Lithographic Evaluation using fine p-beam



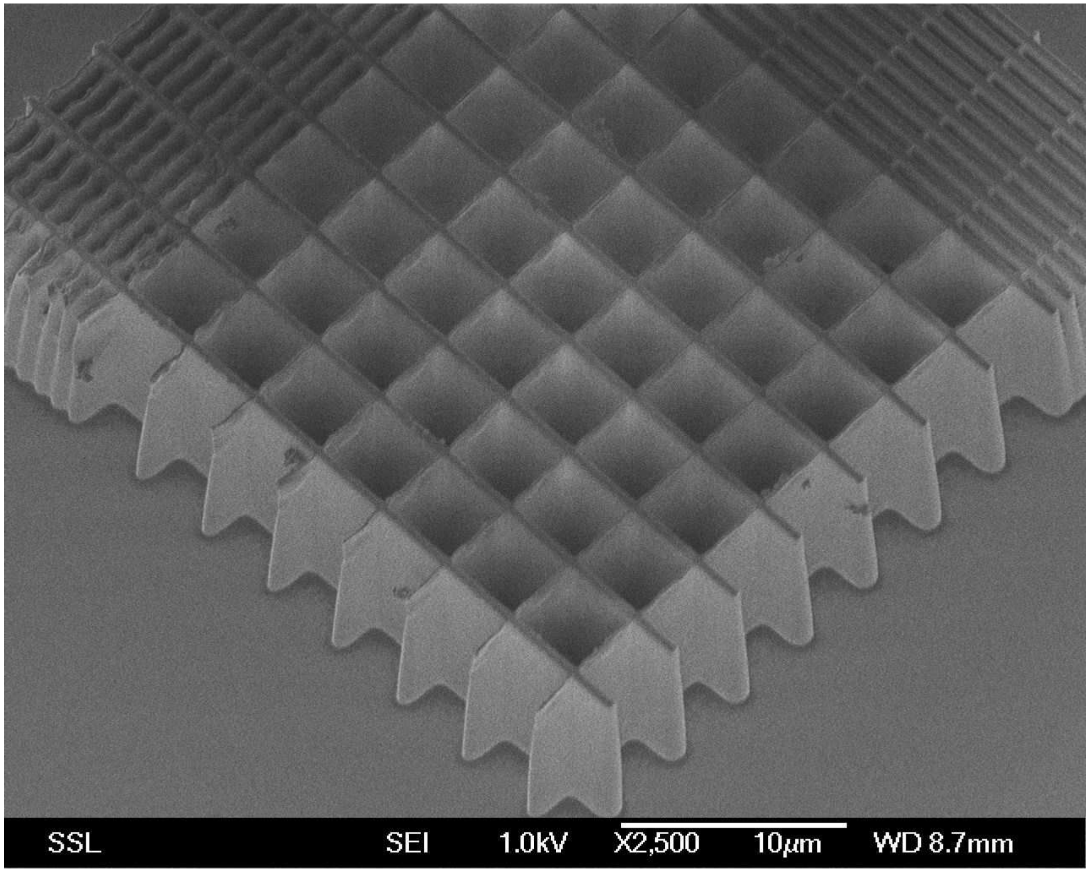


Top view of PBW double line irradiation on TADEP resist.
Line width ~**110nm** in X-direction.
Resist thickness ~2.0 μm
Aspect ratio: 18
Beam size: ~100X200nm
Two pixels pass line

Pitch: 1μm, 4μm

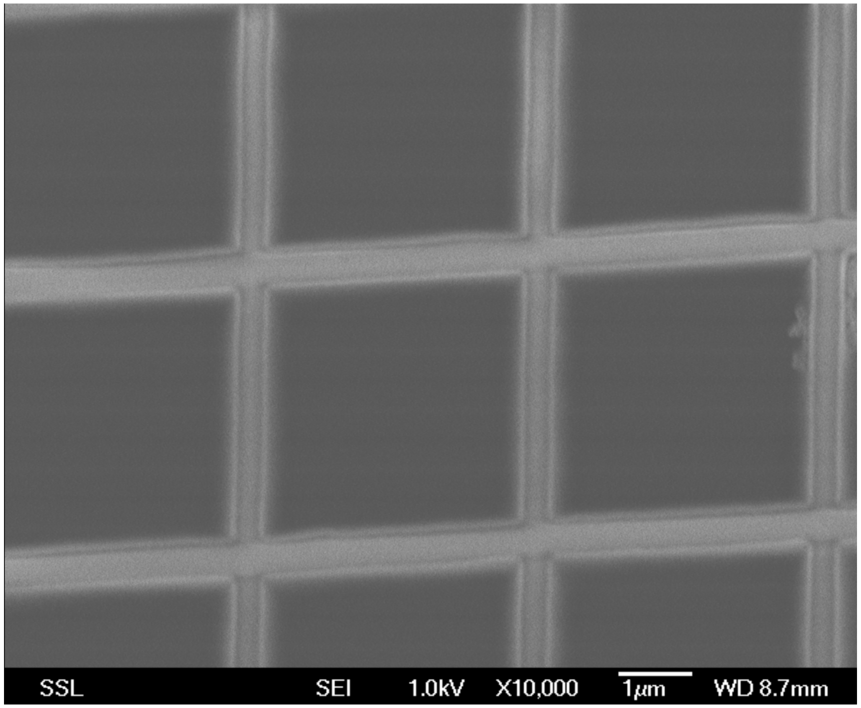


Lithographic Evaluation (III)

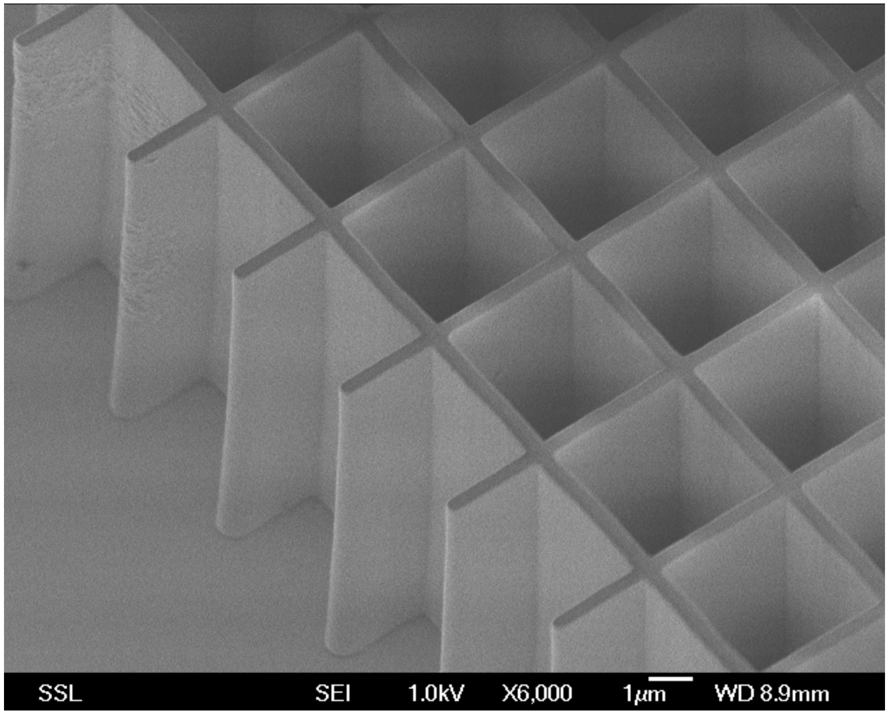


Side view of dense lines by 2MeV PBW on TADEP resist.
Resist thickness ~11.0 µm
Beam size: ~100X200nm
Two pixels pass line
Pitch: 1µm, 4µm

Lithographic Evaluation (IV)

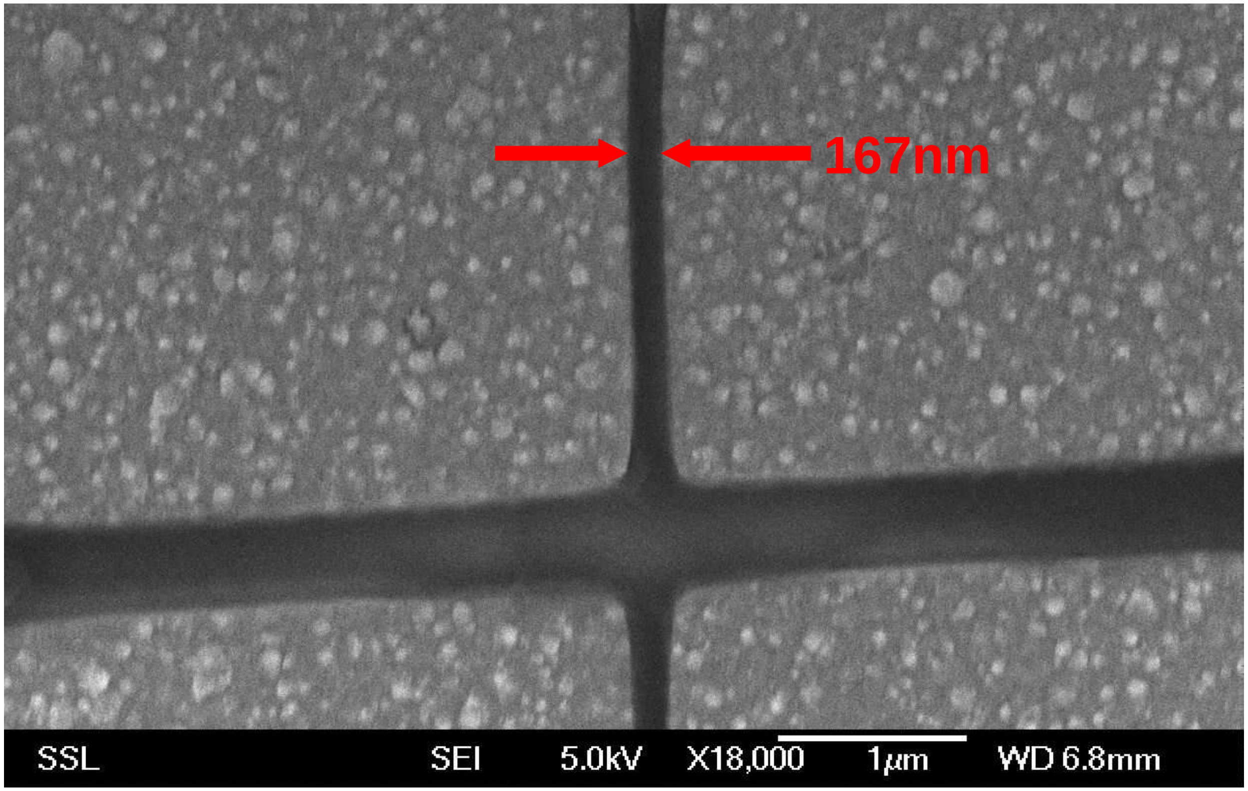


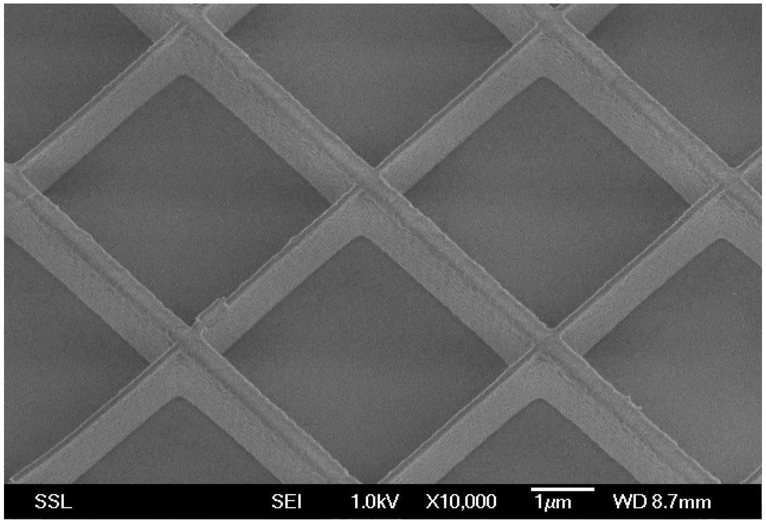
Top view of PBW double line irradiation on TADEP resist. Line width **280nm** in X-direction.



Side view of the pattern. Resist thickness 12μm, aspect ratio: **42**. Beam size: 200nm in X-direction

Electroplating results





Side view of Ni plated on gold features.
Ni thickness 0.8μm

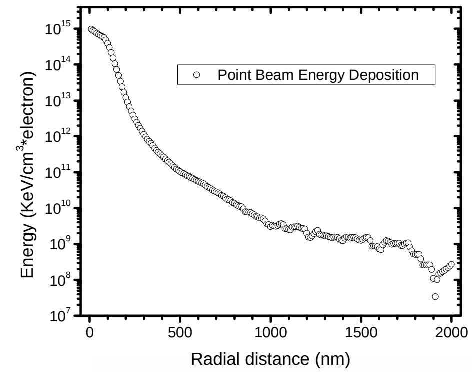
On the right side the resist pattern

Presentation Outline

- Conventional HAR Patterning Technologies
  - X-Ray lithography (XR-LIGA)
  - I-line lithograpy (UV-LIGA)
- Proton Beam Writing (PBW)
  - Principle of operation
  - Advantages & disadvantages
  - Typical results
- Typical HAR Resists
  - PMMA
  - SU-8
- TADEP resist
  - Formulation
  - Physicochemical properties
  - Formulation & processing optimization
  - Lithographic results
  - Electroplating
- **PBW simulation**
  - Simulation of Proton beam – Matter interaction
  - Simulation of the thick polymeric films patterning
- Conclusions

PBW simulation flow-chart

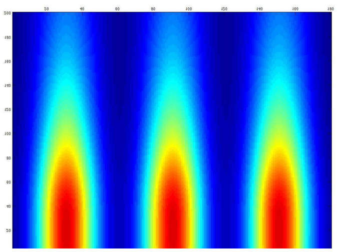
1. Point proton beam simulation
2. Convolution with Gaussian Profile
3. Realistic proton beam simulation
4. Convolution with Layout
5. Energy deposition on resist
6. Thermal processing, PEB simulation (only for CARs*)
7. Development simulation



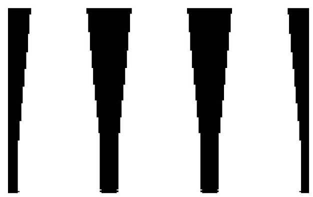
Point Beam exposure

Layout

(top view)



Energy deposition (cross section)



Resist Profile (development)

* **P-RES5** "Stochastic simulation studies of molecular resists for the 32nm technology node"

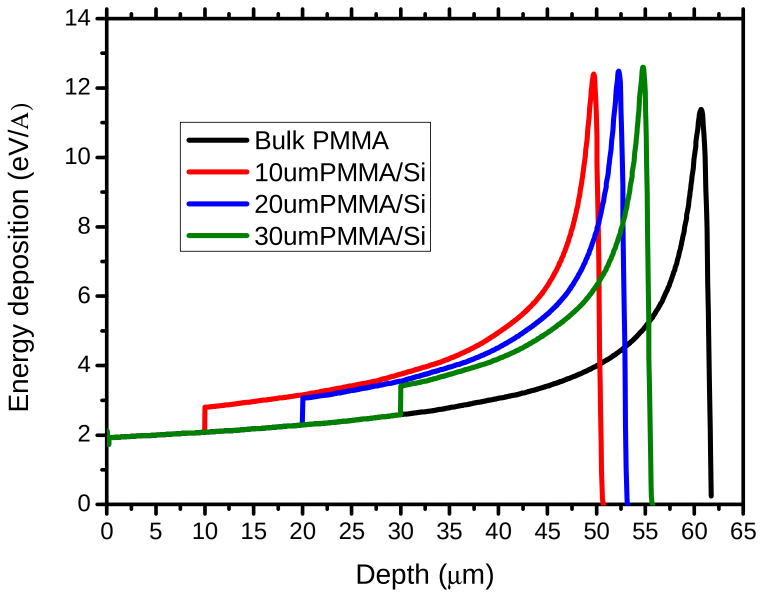
Proton Beam – matter interaction simulation

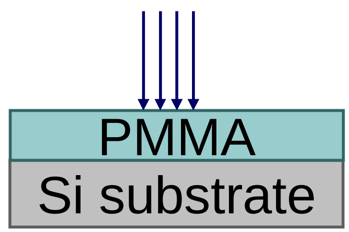
- The formalism adopted for simulating protons propagation is that of **TRIM / SRIM** [1]. At high energies, we have decided, for the sake of the computer efficiency, to base the calculations on the **Coulomb** potential [2].
- Stopping powers at high energies were calculated according to **Bethe's** theory
- At low energies, electronic stopping powers were obtained from experimental data, closely related to the empirical fitting formulas developed by **Andersen** and **Ziegler**.
- The nuclear stopping power, which is important only at very low energies, was obtained by the method of **Everhart** et al [3].

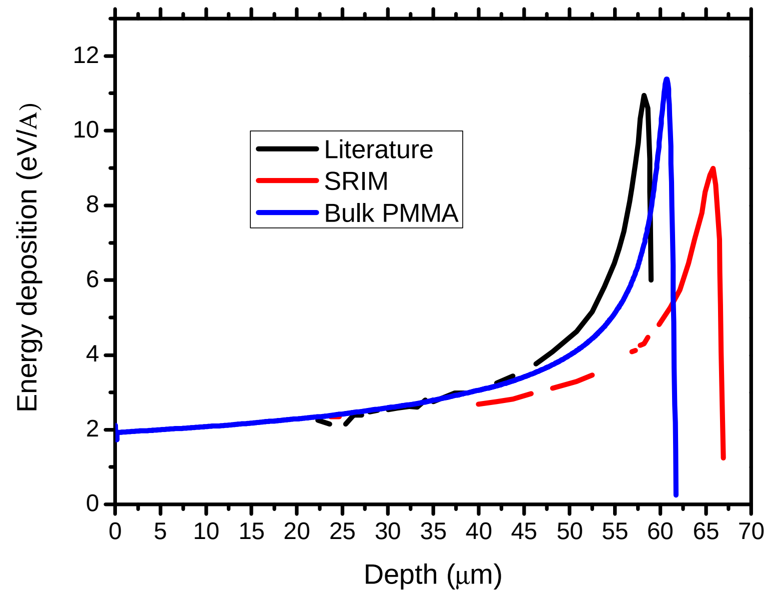
[1] J. Biersack, L. Haggmark, Nucl. Instr. and Meth. 174 (1980) 257.
[2] J. F. Ziegler, J. P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, The Stopping and Ranges of Ions in Matter, Vol. 1, Pergamon Press Inc., 1985.
[3] Stopping Powers and Ranges for Protons and Alpha Particles, International Commission on Radiation Units and Measurements, Report 49, 1993.

imel NCSR Demokritos CIBA

PBW simulation results (energy deposition)







Monte-Carlo (MC) simulation: Energy deposition vs. depth for various resist films.

Proton beam: 2MeV

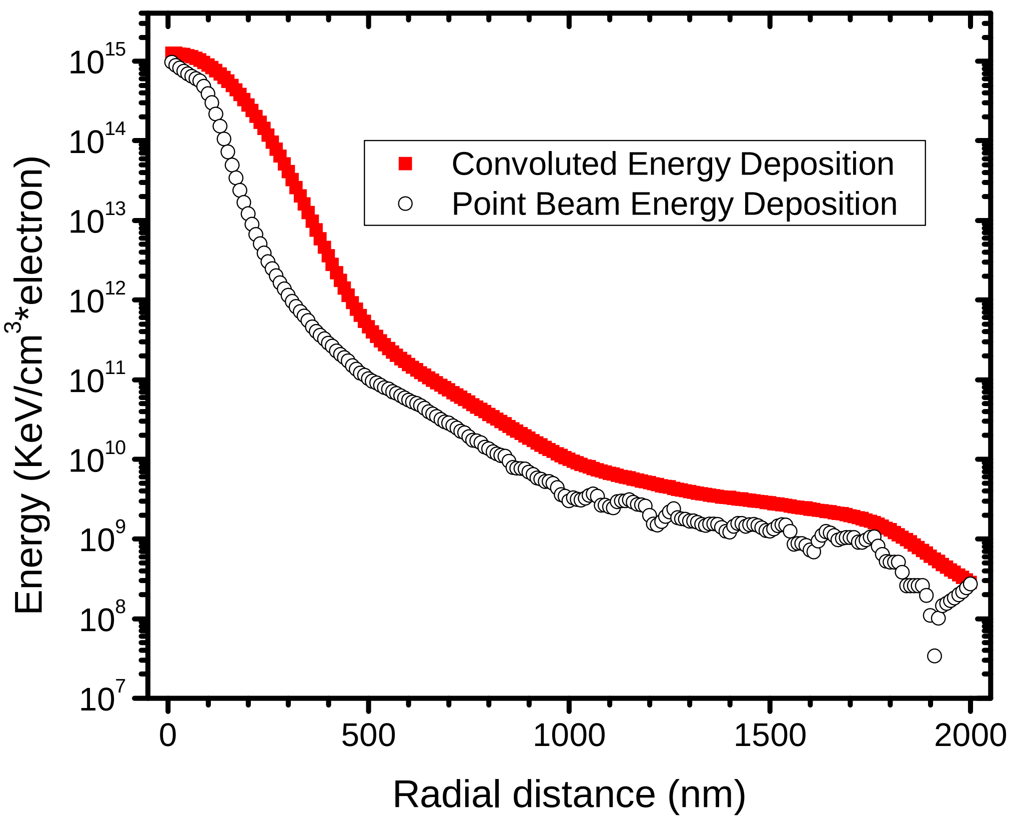
Simulation Dz=50nm

Comparison of the MC simulation results in bulk with the literature and SRIM

Proton beam: 2MeV

Simulation Dz=50nm

PBW simulation results (convolution)



Energy deposition due to point beam and gaussian proton beam at the resist (10μm)/substrate interface (Beam diameter 100nm)

PBW simulation results (layout level)

- ☐ Proton beam irradiated
- ■ Unexposed area

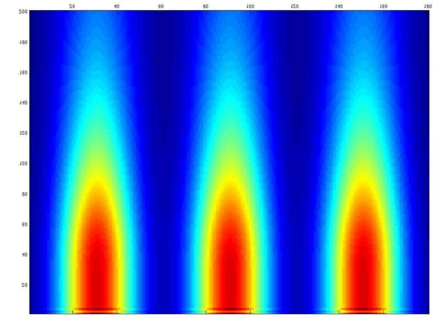
200nm lines / 400nm spaces

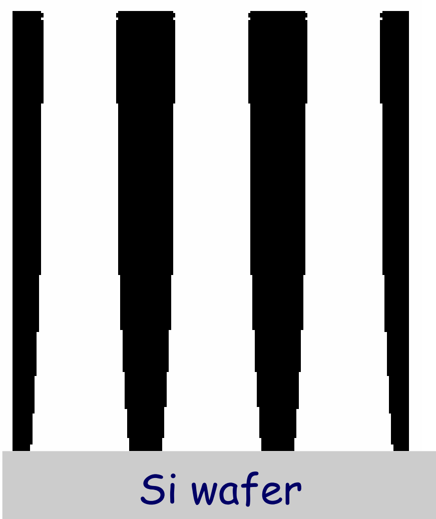
Proton Beam Diameter 100nm

Film Thickness 10μm

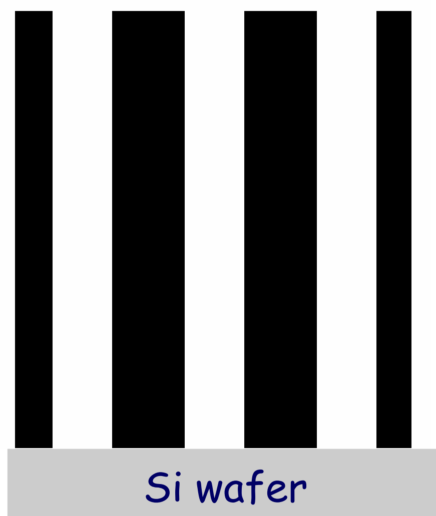
Top view (layout)

Energy deposition (cross section)





Threshold: 0.01 x G



Threshold: 0.1 x G

Cross-section after development (simulation)

Conclusions

Proton Beam Writing proved a powerful micro/nano machining tool, resolution depending on the beam size.

The strippable, aqueous base developable TADEP resist proved adequate for high aspect ratio nanomachining

Dense features with vertical & smooth sidewalls were revealed:

*Thickness **2μm**, Linewidth **110nm**, Aspect ratio **18***

*Thickness **12μm**, Linewidth **280**nm, Aspect Ratio **42***

Successful Ni electroplating is showed demonstrating the stripping capability of TADEP resist

Simulation software for proton beam writing is under development

Acknowledgments

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THANK YOU FOR YOUR ATTENTION