IMI-NFG's Mini Course on Chalcogenide Glasses

Lecture 11

Photonics applications 5: photoresists

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Resources:

1. IMI-NFG Video Lectures by Prof. Vlcek: Glasses for Lithography & Lithography for Glasses http://www.lehigh.edu/imi/TutAdv_R.htm
2. A. Kovalskiy et al. Chalcogenide glass e-beam and photoresists for ultrathin grayscale patterning, J. Micro/Nanolith. MEMS MOEMS 84, 043012 (2009)
3. H. Jain and M. Vlcek, Glasses for lithography, J. Non-Cryst. Solids 354 (2008) 1401–1406

Lithography:

Original: **From Greek *lithos*, 'stone' + *graphein*, 'to write‘, is a method for printing using stone**

Modern Technology: **Writing of a pattern or 3D relief images in film with the aim of transferring them subsequently to the substrate**

Microlithography **– patterning method which allows fabrication of features smaller than 10 µm**

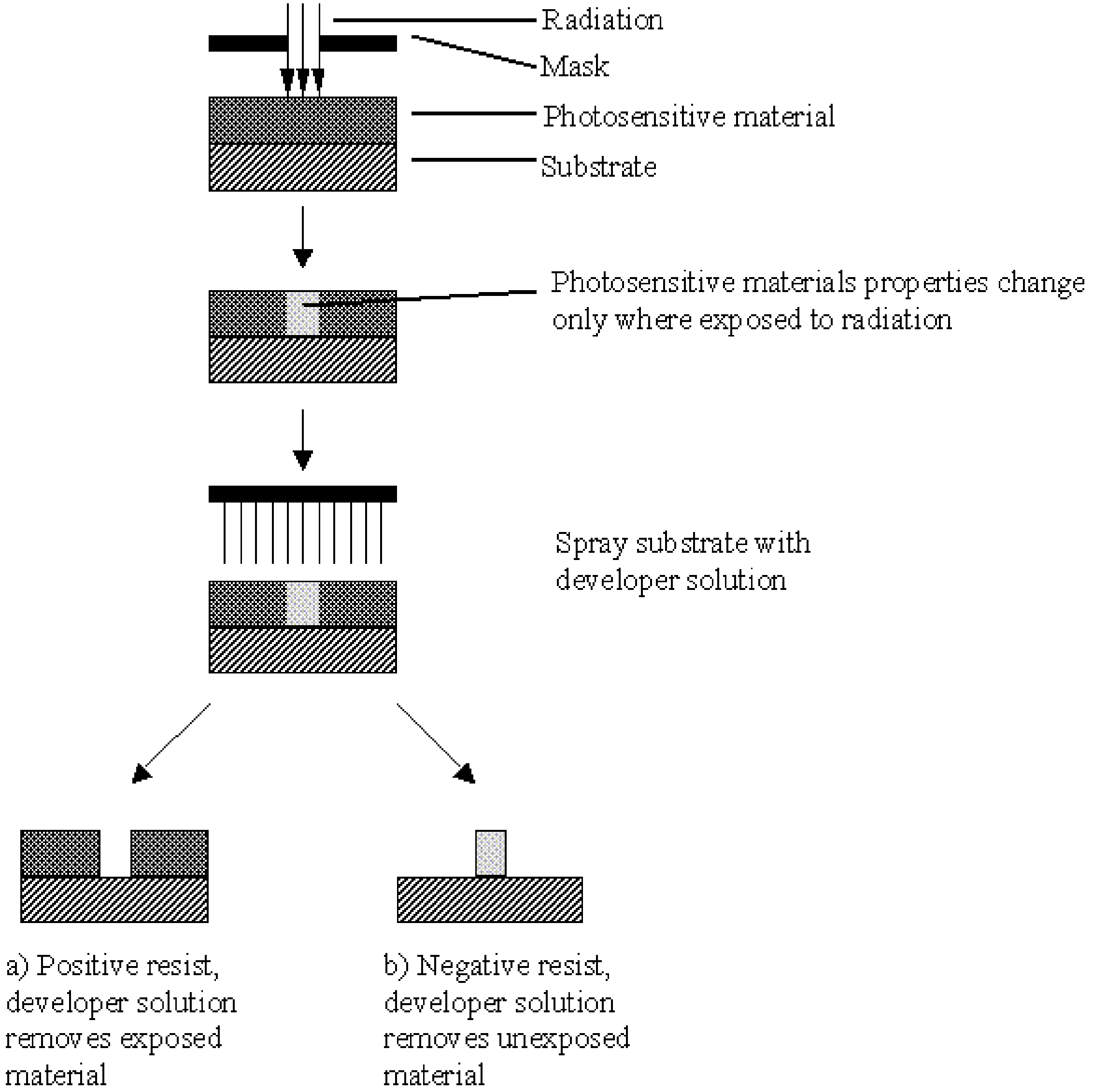
Nanolithography **– patterning on a scale smaller than 100 nm**

Contact and/or proximity lithography **– patterning with photomask in direct contact with resist-coated substrate and/or small gap between them**

Maskless lithography **- no mask is required to generate the final pattern e.g.:**
- ***electron beam lithography*** **– final patterns are created from digital design; computer controls the scan of an e-beam across a resist-coated substrate**
- ***interference lithography***

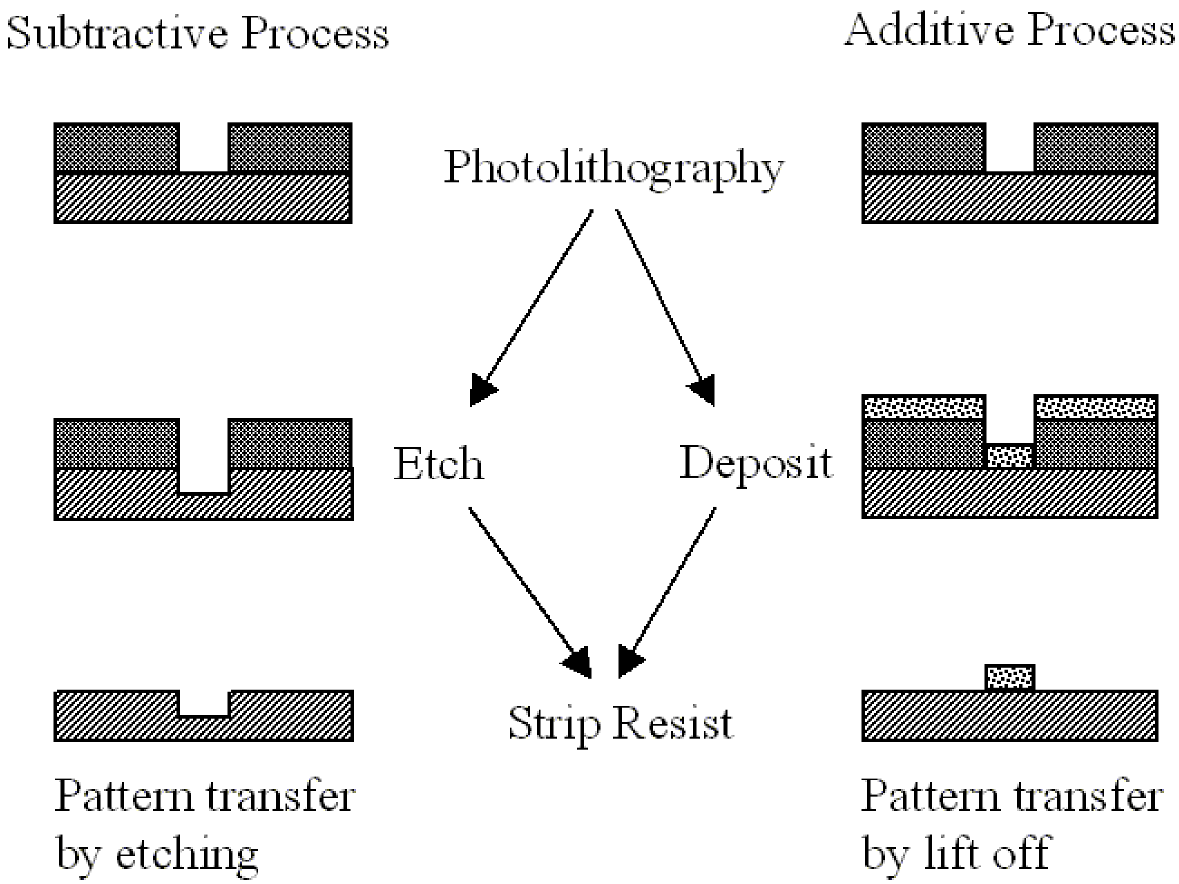
Components of modern lithography

1. An exposure (irradiation) source
2. A mask and/or computer controlled scan of suitable beam across resist-coated substrate
3. A resist that stores the pattern
4. Know-how of a series of fabrication steps that would accomplish pattern transfer from the mask to resist and subsequently to substrate on which device is to be fabricated



http://www.memsnet.org/mems/processes/lithography.html

Pattern transfer from photoresist to substrate



a) *Pattern transfer from patterned photoresist to underlying layer by etching*
b) *Pattern transfer from patterned photoresist to overlying layer by lift-off*

Most important properties of any resist

Sensitivity to some radiation and proper technology of selective etching (simpler is better)

Resistant to agents used for substrate etching

High resolution – nano is better

Easy deposition – homogenous in properties and thickness

Radiation-induced processes in amorphous chalcogenides

Structural changes:

- *changes of local atomic configuration*
- *polymerization – creating new bonds*
- *phase changes, including crystallization*

Physico-chemical changes:

- *decomposition*
- *photo-vaporization*
- *photo-dissolution of certain metals*
- *thermoplastic changes*

All these processes can result in changes of optical and physico-chemical properties ⇒ Suitable for lithography resist

Exposure with suitable radiation can change chemical resistance

What does it mean „suitable radiation“?
Band gap light (≈ 1 – 2.3 eV)
UV or even visible light
e - beam
flux of ions
X –rays ...

Both dry and wet etching can be applied

- ***Wet etching – all photoinduced processes can be applied***
- ***Dry etching – usually photo-dissolution of certain metals is applied***

Amorphous chalcogenides

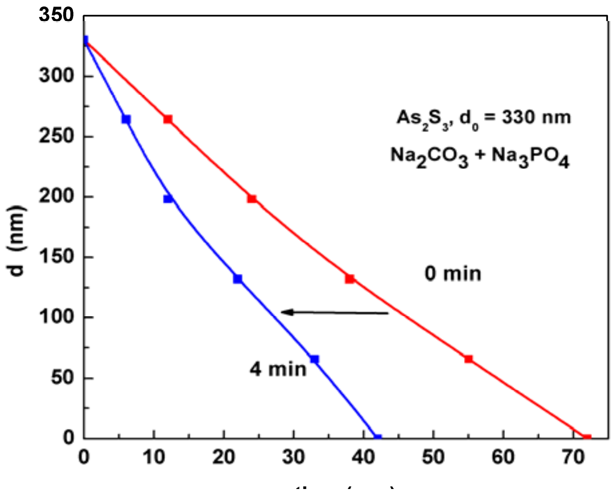
insoluble
in acid solutions

relatively well soluble
in alkaline solvents

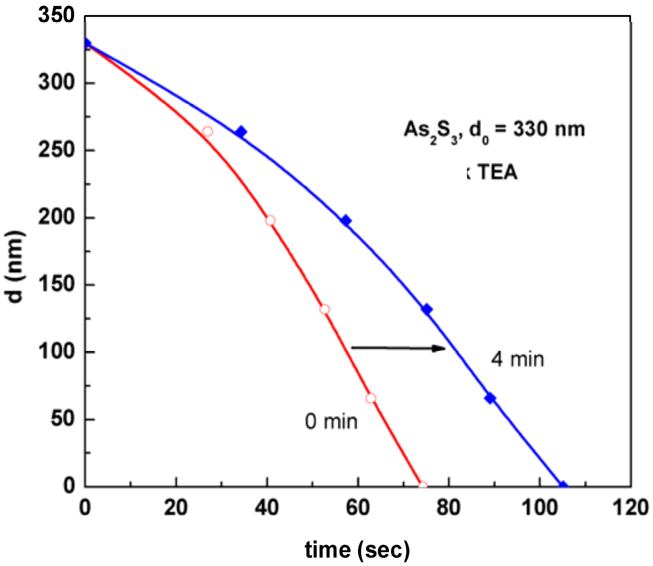
- Dissolution rate in alkaline solvents can be influenced by exposure

- Both positive and negative etching can be achieved (even without Ag diffusion)

Aqueous vs. organic solvent



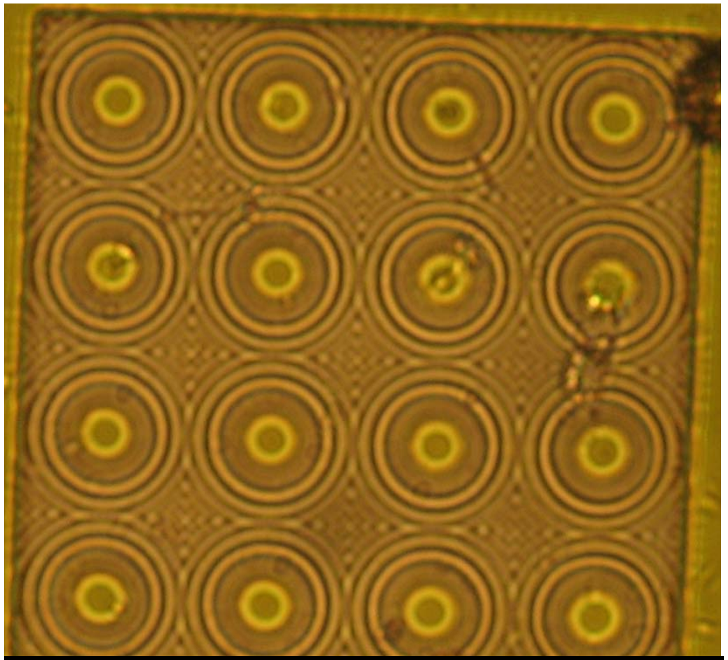
Aqueous base
⇒
Positive etching



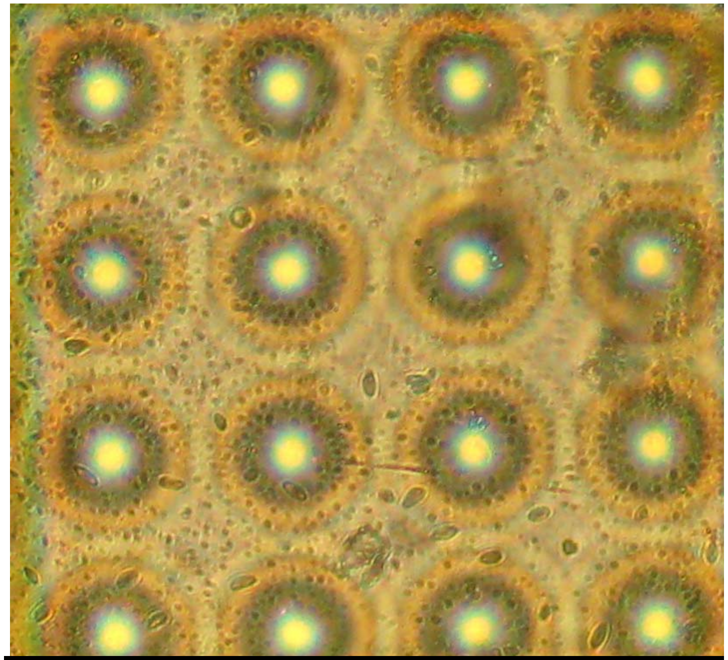
Organic amine base
e.g. triethylamine
⇒
Negative etching

Thinnest Fresnel Lens Array for IR Imaging

120 μm

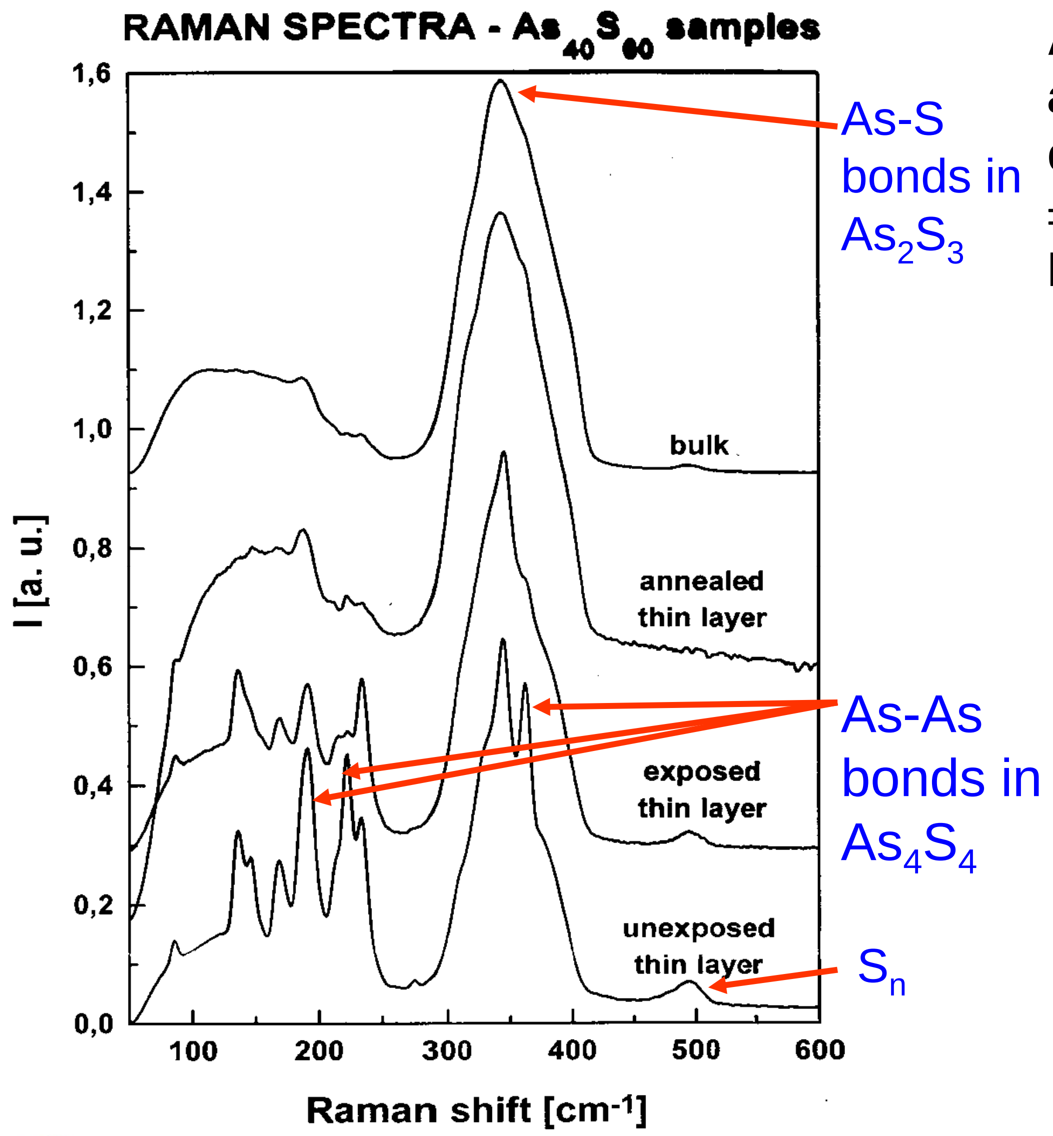


Focused on surface



At focal point ~300 μm

Raman spectra of ChG films and bulk



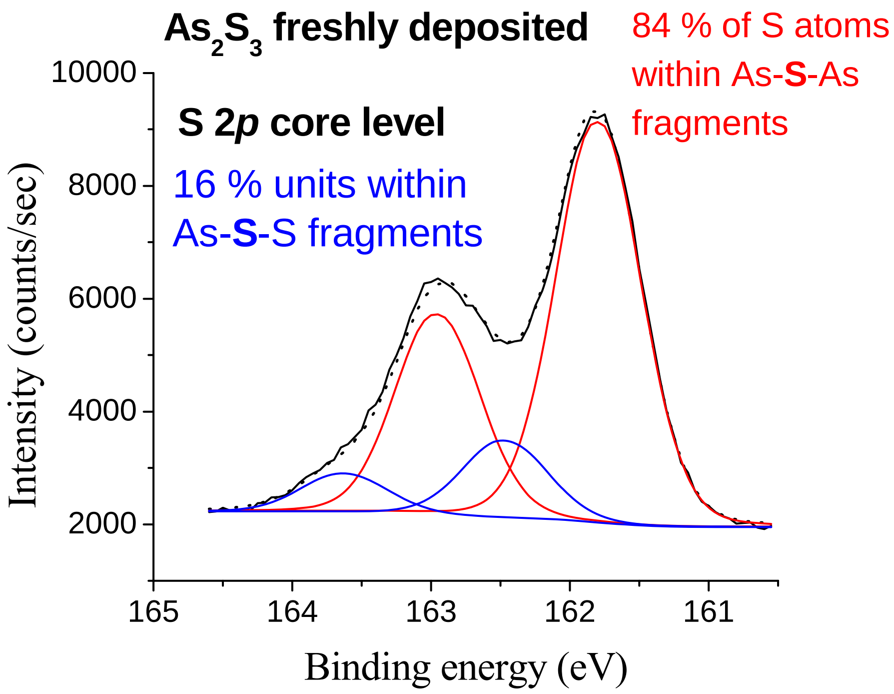
As deposited films contain As_4S_4 and S_n fragments, which tend to disappear by light or heat.

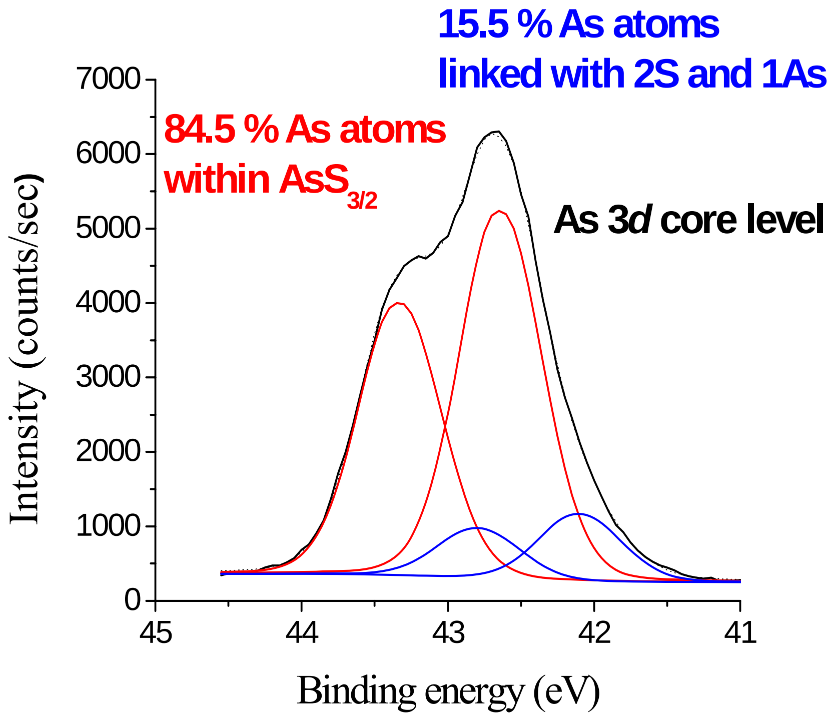
⇒

Increase in etching rate

Structure of ChG thin films by high resolution XPS

As_2S_3 thin films deposited inside of XPS chamber without contact with air

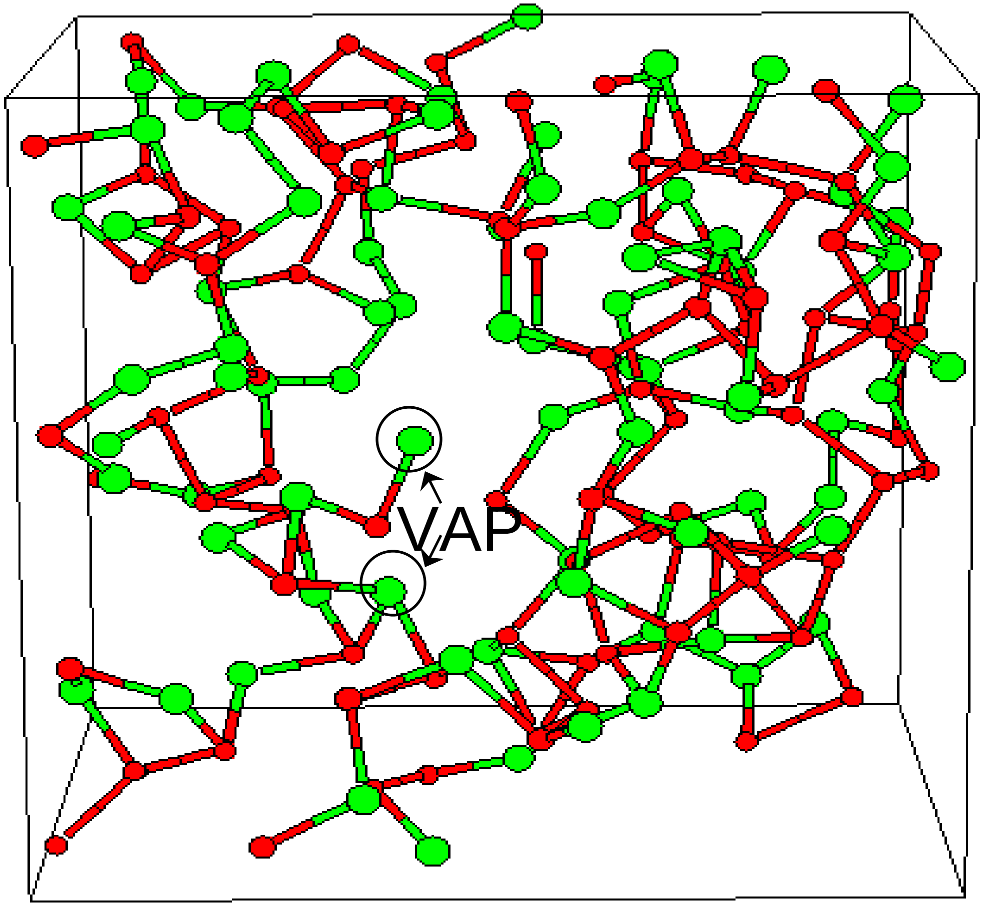




Films have significant fraction (~16%) of S and As atoms in wrong bonds.

Precision for such estimation depends on the parameters of spin orbit splitting

First Principles MD simulation of a-As_2Se_3



Li and Drabold (2001)

🟩 Se atom

🟥 As atom

Chemical disorder:
As-As and Se-Se
Coordination defects:
Se_3^+, Se_1^-, As_4^+, As_2^-
Valence alternation pairs (VAP):
$2\ Se_2^0 \rightarrow Se_3^+ + Se_1^-$

	Chemical disorder	Coordination defects
As	**High**	**Low**
Se	**High**	**High**

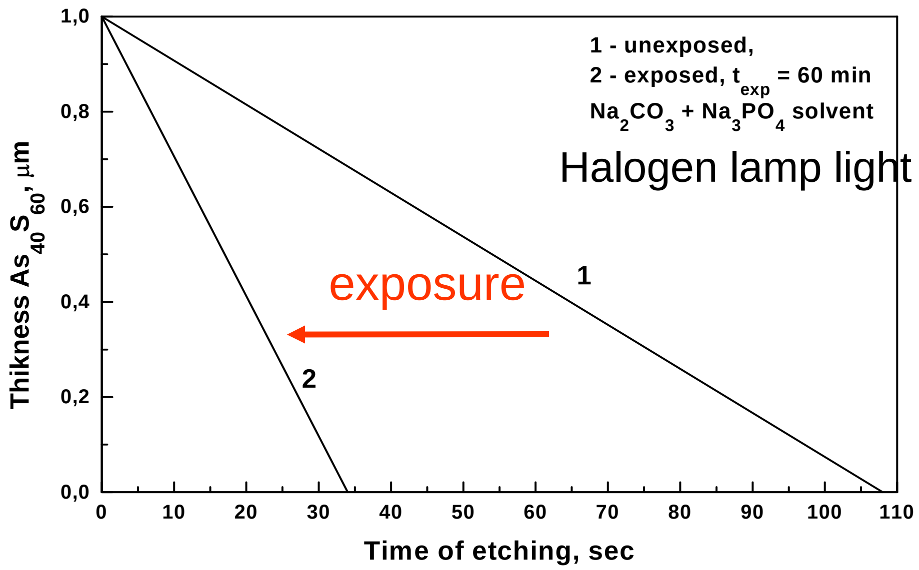
Basic Mechanism of Positive Photo-etching

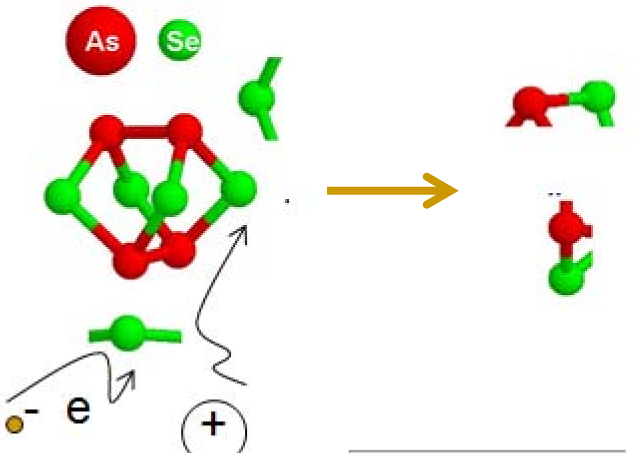
1. As_4S_4 crystals dissolve much more slowly than As_2S_3crystals

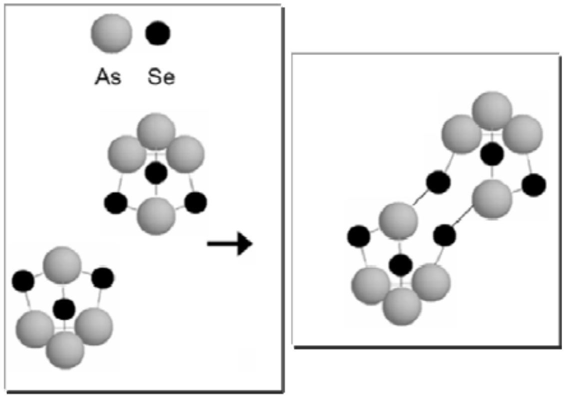
+

light

2. $As_4S_4 + S_n$ (in AP- As_2S_3 film) → As_2S_3 (in exposed film)







Mechanism of NEGATIVE selective etching in non-aqueous amine based solvents

Amines can promote the cleavage of sulfur rings (or chains)

$$R_3N + S_8 = R_3N^+S_8^-$$

Exposed parts – ammonolysis of heteropolar bonds (slow process)

$$As_2S_3 + 6\,(C_2H_5)_2NH = [(C_2H_5)_2NH_2]_3AsS_3 + As[(C_2H_5)_2N]_3$$

Unexposed part – breaking of polymeric network through homopolar bonds (faster process)

$$(C_2H_5)_2NH + S_n = (C_2H_5)_2NH^+S_n^-$$

$$(C_2H_5)_2NH^+S_n^- + As_2S_{4/2} = (C_2H_5)_2NH_2^+S^-AsS_{2/2} + (C_2H_5)_2NAsS_{2/2}$$

S.A. Zenkin, S.B. Mamedov, M.D. Mikailov, E. Yu. Turkina, I.Yu. Yusupov: Fizika i Khimiya Stekla 23 (5) (1997) 393

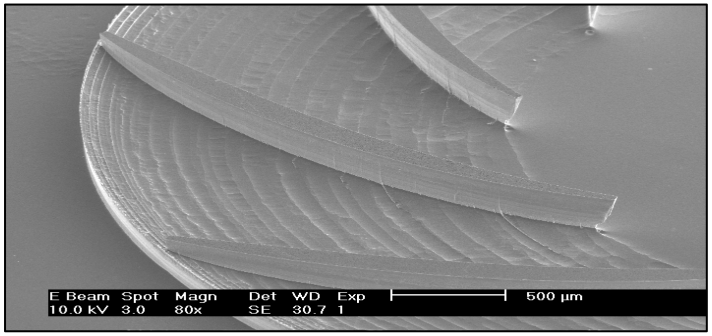
Parameters influencing selectivity of wet etching

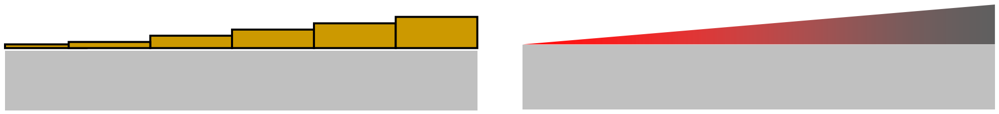
- Sample composition, method and conditions of thin film preparation
- Prehistory of sample – virgin vs. annealed
- Exposure conditions (I, λ, T, τ, environment...)
- Etching conditions (composition of etching bath, pH, temperature..)

Emerging needs: dry, grayscale lithography

Motivation:

Gray scale profiles in photoresist film, for example development of microturbine compressor with variable height blades

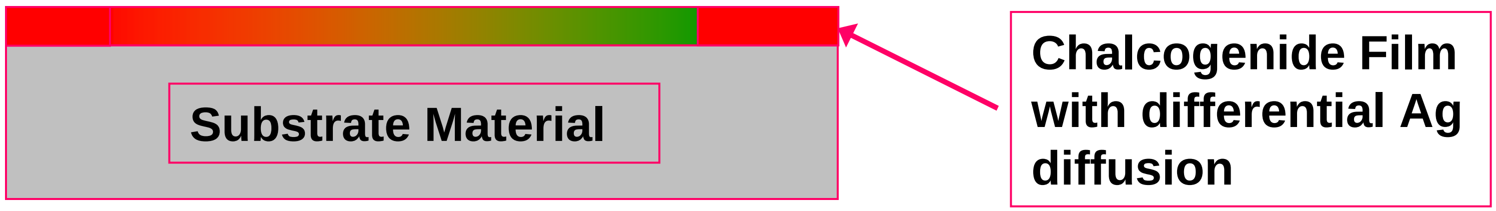




Current Desired

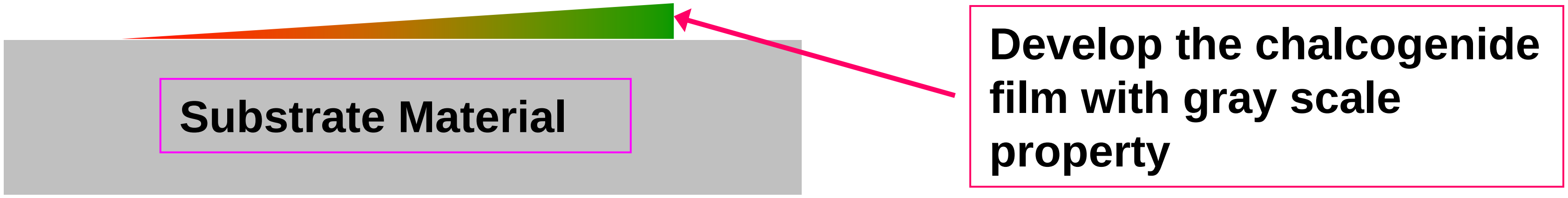
Grayscale chalcogenide negative photoresist

1. **Diffuse Ag into chalcogenide film through modulated halogen lamp light exposure**
2. **Remove excess of Ag for negative resist**



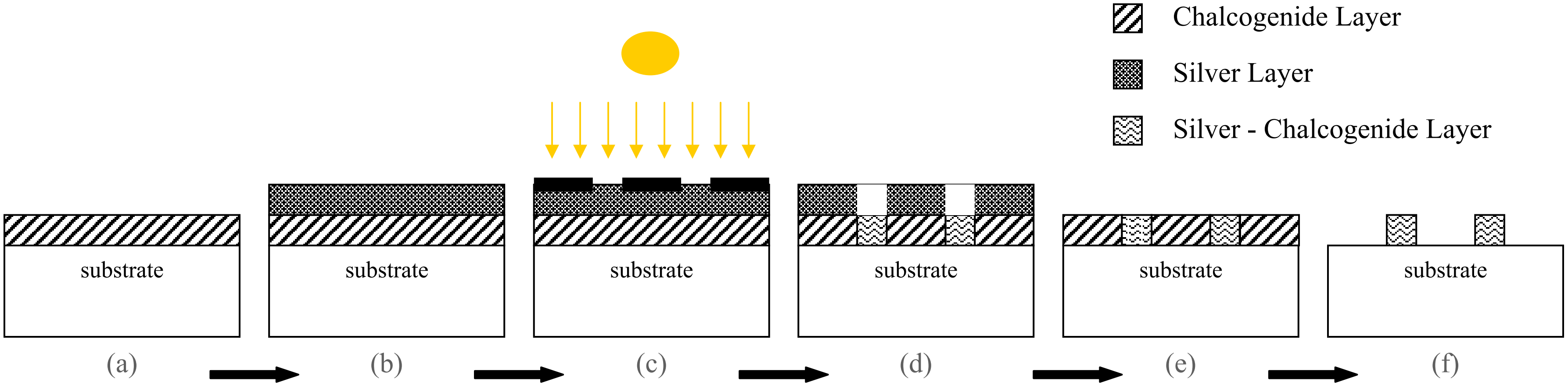
Chalcogenide Film with differential Ag diffusion

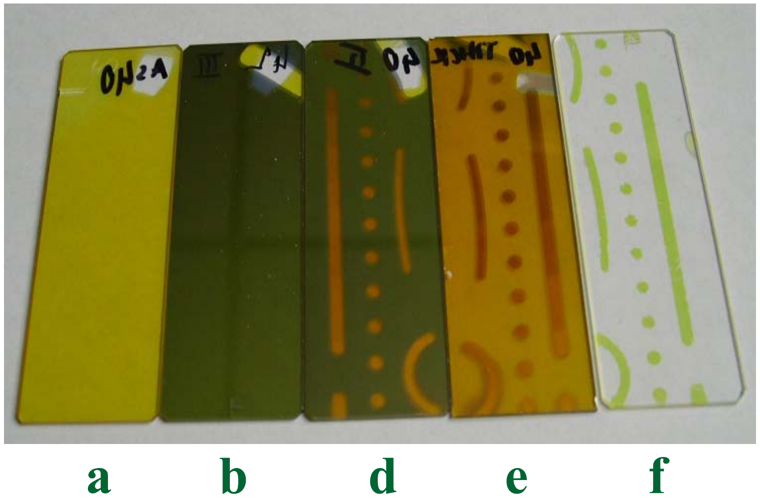
3. **Develop the chalcogenide film**
   1. **Etch rates vary due to diffused Ag gradient**
   2. **Reactive Ion Etching (RIE) – good dimensional control**



Develop the chalcogenide film with gray scale property

Photodoping with Ag for Enhanced Selectivity





(a) Deposition of chalcogenide layer

(b) Deposition of silver layer

(c) Exposure through mask

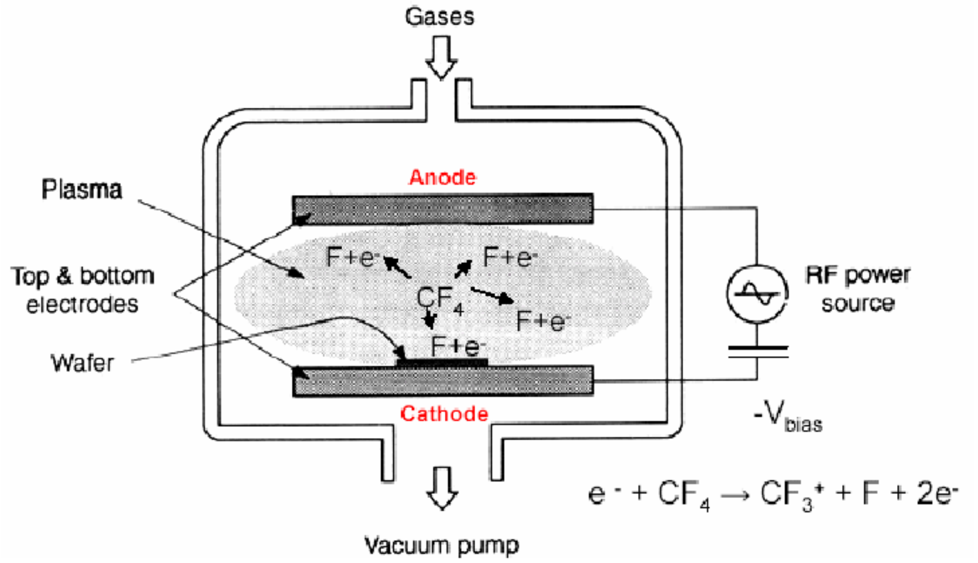
(d) Silver diffusion

(e) Removal of remaining silver

(f) Removal of chalcogenide regions to create photoresist

DRY ETCHING

Plasma of ionized gases used to blast away atoms from the surface of the sample. (Also known as plasma etching)



$e^- + CF_4 \rightarrow CF_3^+ + F + 2e^-$

Harsh conditions in plasma require hard photoresist ! including:

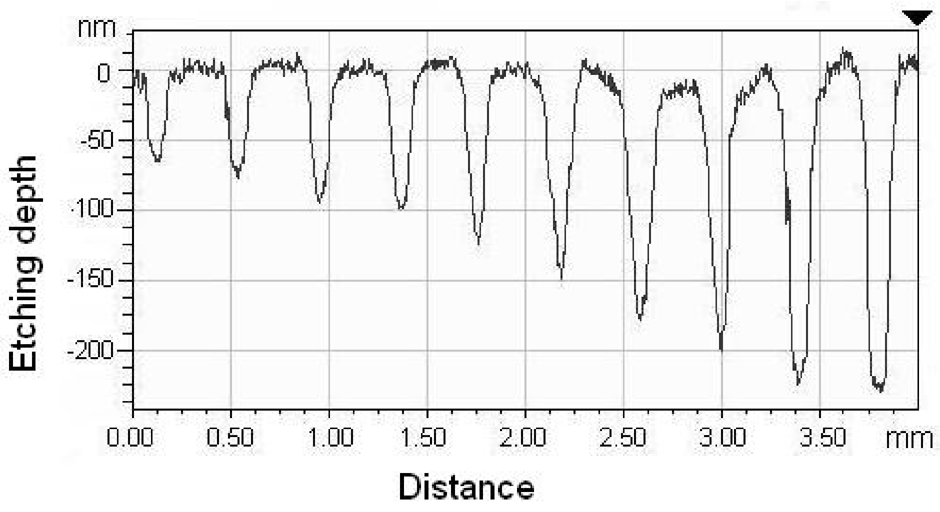
- **high contrast of pattering**
- **resistance to aggressive, ionized gases**

Certain metals are usually added to ChG photoresist – Why?

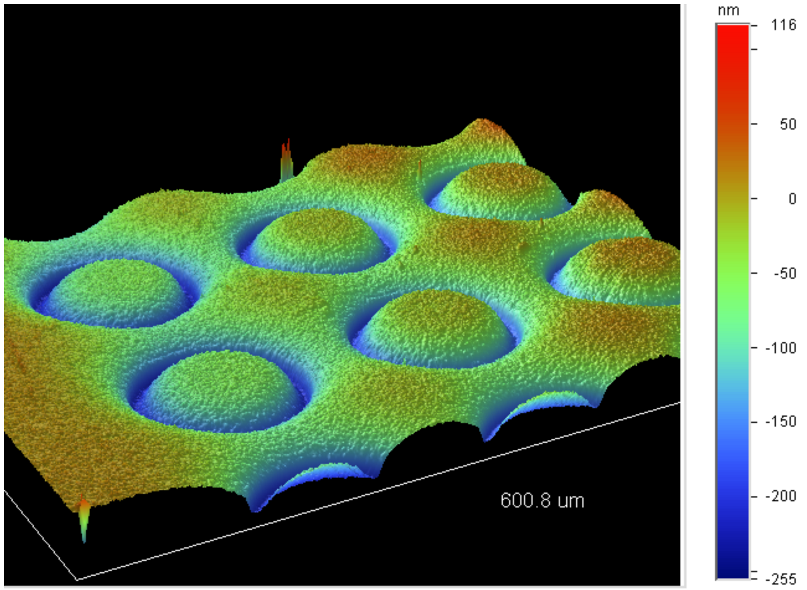
Combine <u>photostructural and compositional changes</u> from photodiffusion of metal (mainly Ag) in ChG.

www2.ece.jhu.edu/faculty/andreou/495/2003/LectureNotes/DryEtching.pdf

- Ag diffuses into As-S glass in step like fashion
- depth of diffusion - function of exposure dose



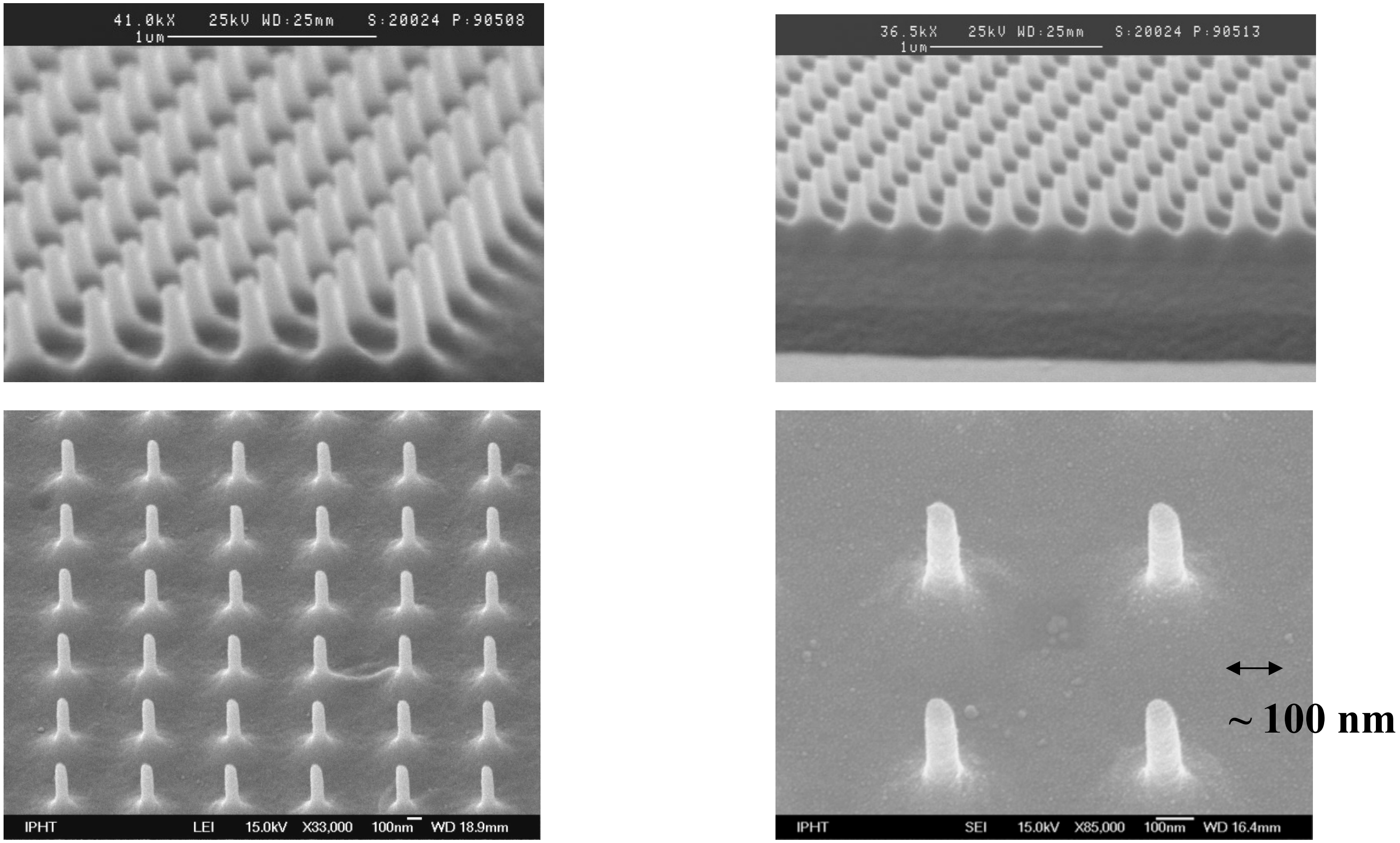
Profilogram demonstrating the change of etching depth with gradual variation of transparency of mask fragments.



Optical Profiler image demonstrating the possibility of smooth shaping with lens-like mask by photoinduced Ag diffusion into As_2S_3 film with following dry etching (reverse image, depth of etching 200 nm). CF_4 as the etchant gas, with pressure of 100 mTorr, an electrode power of 110 W, CF_4 flow rate of 100 sccm and an etching time of 2 min

A. Kovalskiy, H. Jain, J. Neilson, M. Vlcek, C.M. Waits, W. Churaman, M. Dubey On the mechanism of gray scale patterning of Ag-containing As_2S_3 thin films Journal of Physics and Chemistry of Solids 68 (2007) 920-925

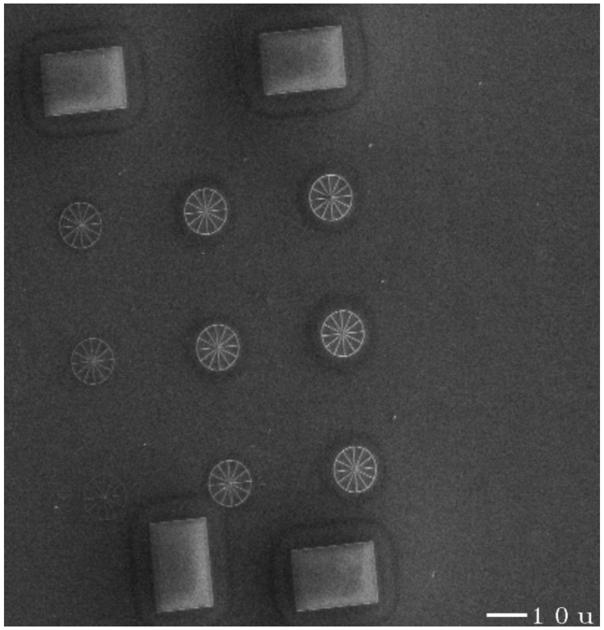
Electron beam wet **nano**lithography

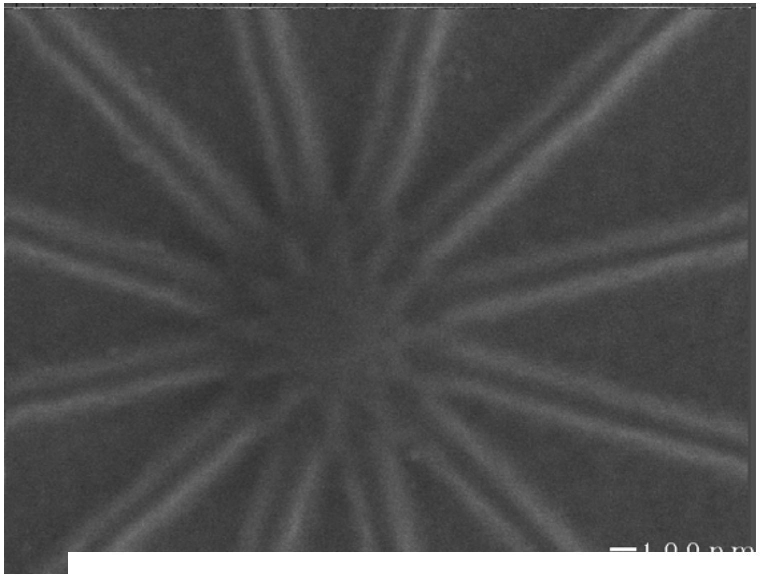


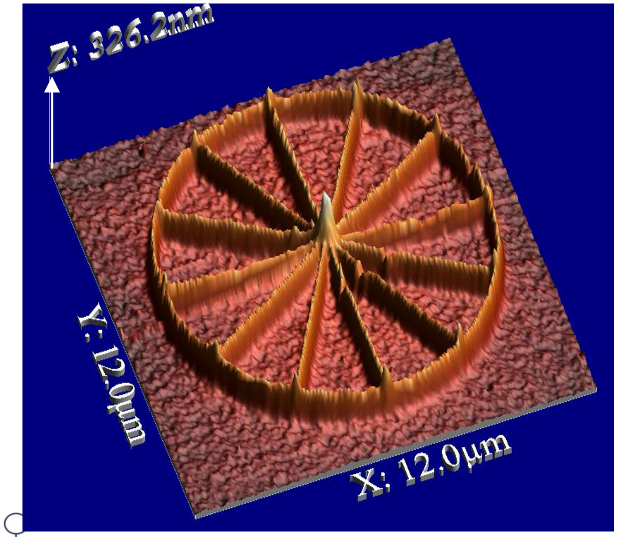
SEM pictures of pillar arrays in quadratic arrangement etched into $As_{35}S_{65}$. (a): diameter 122 nm, depth 410 nm, and period 400 nm (b): diameter 100 nm, depth 410 nm, and period 300 nm (c,d): diameter less than 100 nm, depth 300 nm, and period 350 nm, displayed at different magnifications

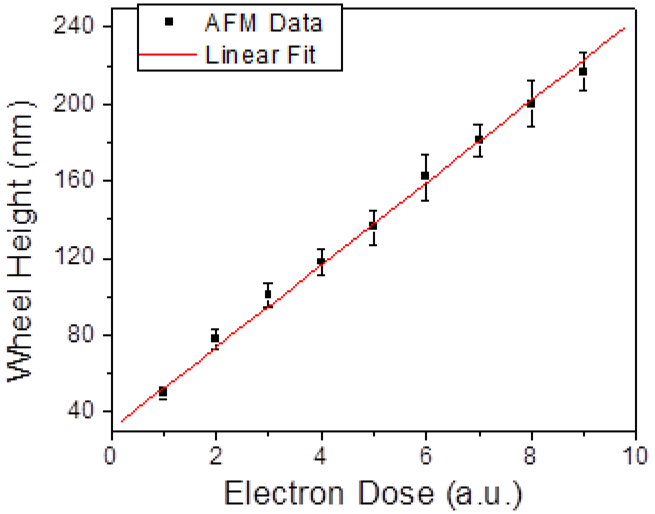
S. Schröter, M. Vlcek, R. Pöhlmann, T. Glaser and H. Bartelt: Proceedings of MOC´04, Jena, Germany, September 2004

High resolution capability





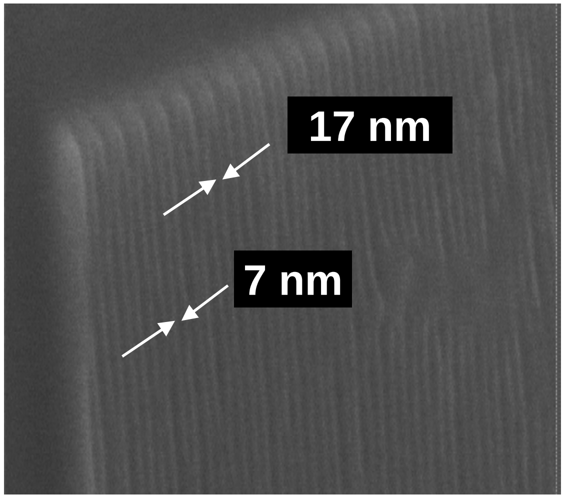




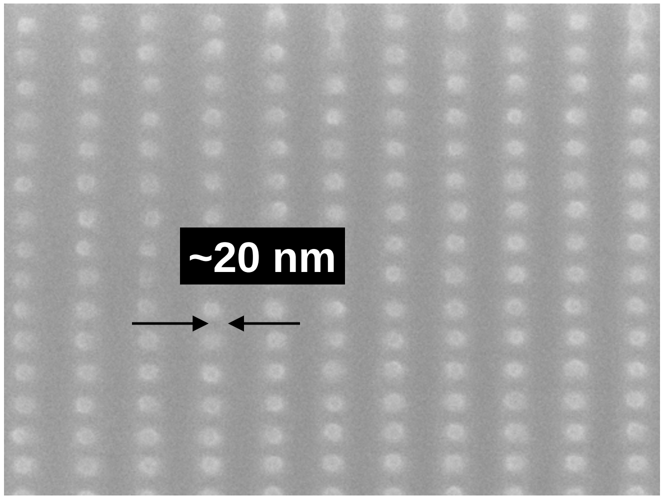
M. Vlcek, H.Jain J. of Optoelectronics and Advanced Materials 8 (6) (2006) 2108 -2111

E-beam Patterning of Chalcogenide Glasses

What is the resolution limit for ChG?



J. Neilson, A. Kovalskiy, et al. J. Non-Cryst. Solids 353 (2007) 1427



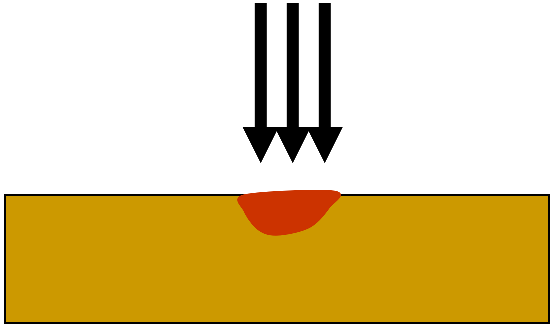
unpublished

Finest structural features on glasses

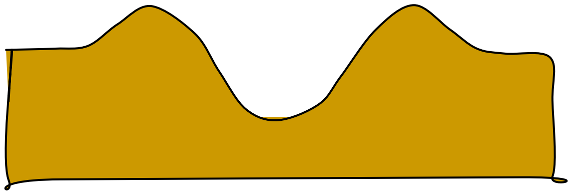
Direct observation of separate e-beam spots

Wet Etching in Amine Solution

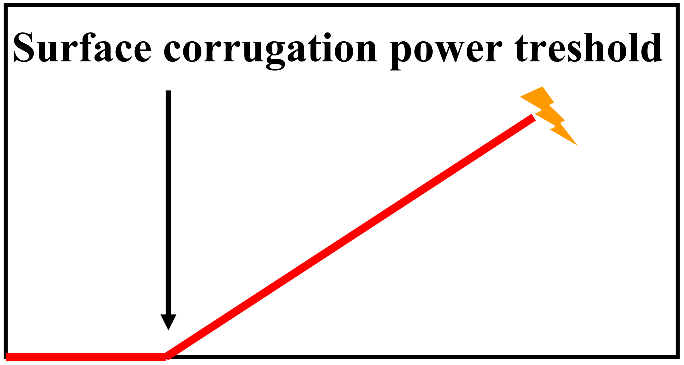
Photoinduced local corrugation by high energy high intensity beam



Local heating + light field driven mass transport

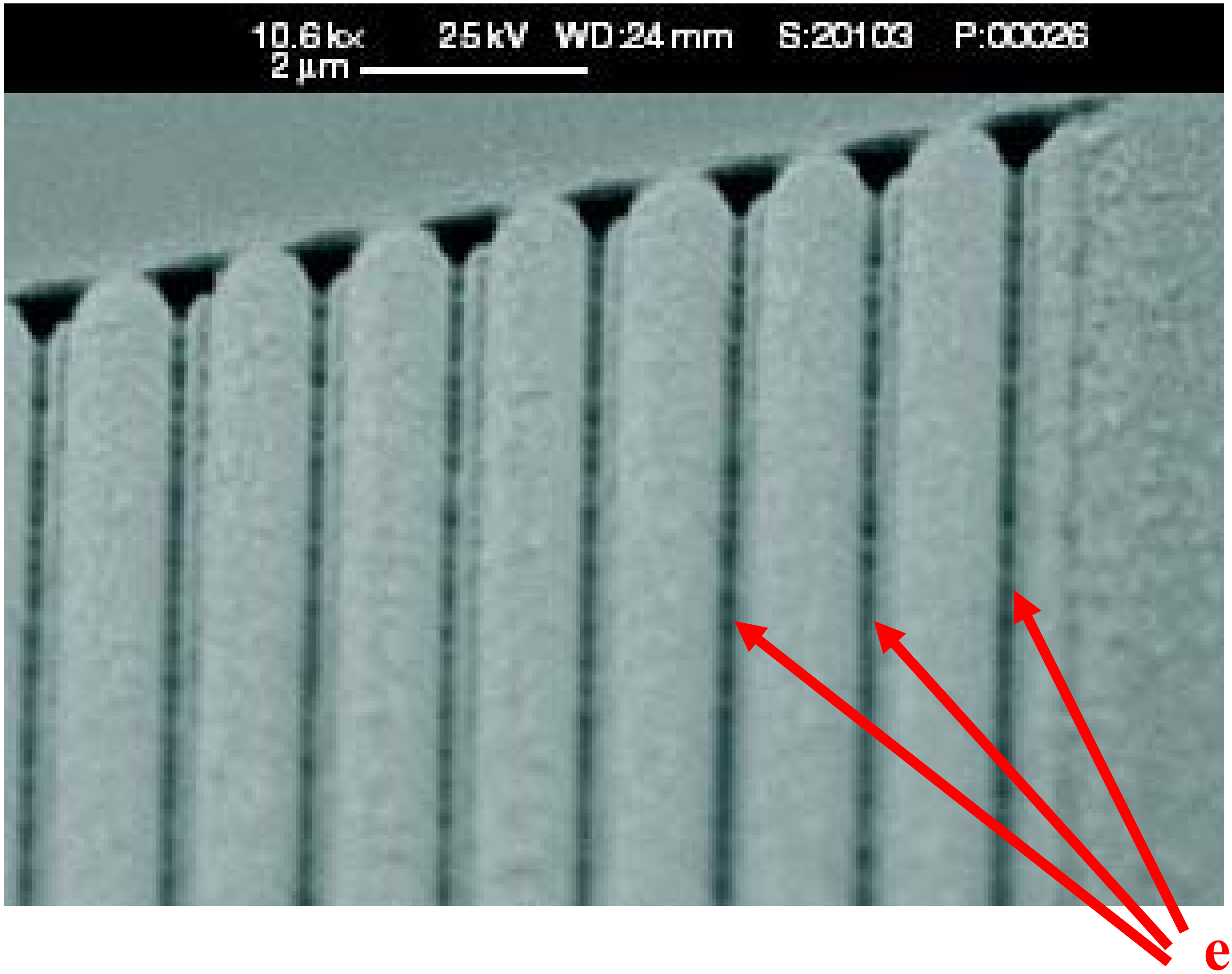


Corrugated result



Surface corrugation power treshold

Laser writer DWL 66-UV, 244 nm – doubled Ar laser

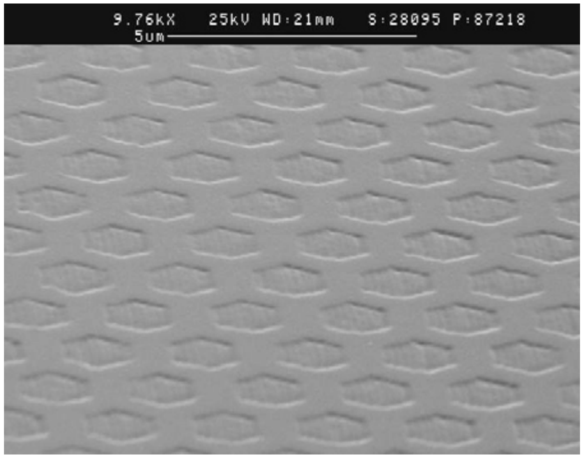


exposed

Grating in $As_{35}S_{65}$ layer with period of 1.28 µm, and grooves of 160 nm bottom width and 640 nm depth, written with beam power of 400 mW at a scanning speed of 30 mm/s

T. Glaser, S. Schröter, S. Fehling, R. Pöhlmann and M. Vlcek ELECTRONICS LETTERS 40 (3) (2004) 176-177

Laser writer DWL 66-UV, 244 nm – doubled Ar laser



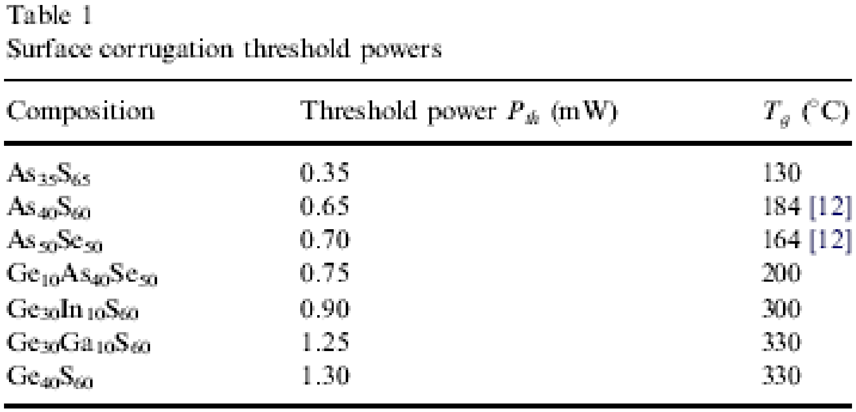
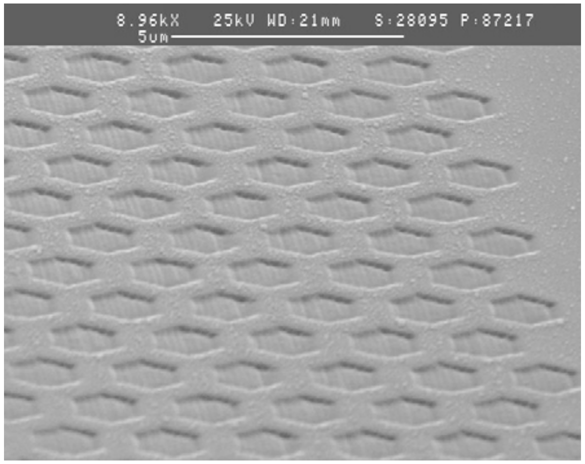
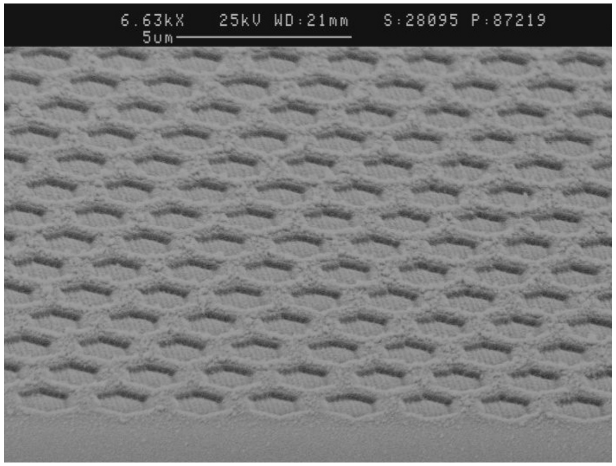


Table 1
Surface corrugation threshold powers

Composition	Threshold power P_{th} (mW)	T_g (°C)
$As_{35}S_{65}$	0.35	130
$As_{40}S_{60}$	0.65	184 [12]
$As_{50}Se_{50}$	0.70	164 [12]
$Ge_{10}As_{40}Se_{50}$	0.75	200
$Ge_{30}In_{10}S_{60}$	0.90	300
$Ge_{30}Ga_{10}S_{60}$	1.25	330
$Ge_{40}S_{60}$	1.30	330





SEM pictures of 2D gratings fabricated by direct DUV laser writing technique and consisting of a trigonal air hole pattern written with a period of 2.2 μm designed to exhibit hexagonal holes of 1.6 μm width across flats in a 700 nm thick layer of $As_{35}S_{65}$ written at 0.4 mW (up), 0.5 mW (left) and 0.8 mW (right) imaged at 75°.

For 0.5 mW the exposed power intensity and dose are 0.7 MW/cm^2 and 2.6 J/cm^2.

S. Schroeter, M. Vlcek, R. Poehlmann, A. Fiserova Journal of Physics and Chemistry of Solids 68 (5-6) (2007) 916-919

Summary

Why Chalcogenide Glasses for Lithography?

- **Sensitive to different radiations ⇒ Greater versatility**
- **Smaller molecular units ⇒ Higher resolution**
- **Much harder than polymers ⇒ Maintains shape**
- **Easier deposition of thin, uniform films ⇒ More accurate transfer of patterns (eliminates interference effects)**
- **Optical functionality ⇒ Etchless resist**
- **Metal photodissolution ⇒ Dry grayscale lithography possible**
- **Much simpler etching, without any other treatments**
- **Resistant to acids ⇒ Easier transfer of patterns in substrates**
- **Both positive and negative resists are possible**

Conclusion:

ChG offer a new more powerful class of photoresists for more versatile lithography than currently available polymer resists