Glasses for lithography and lithography for glasses

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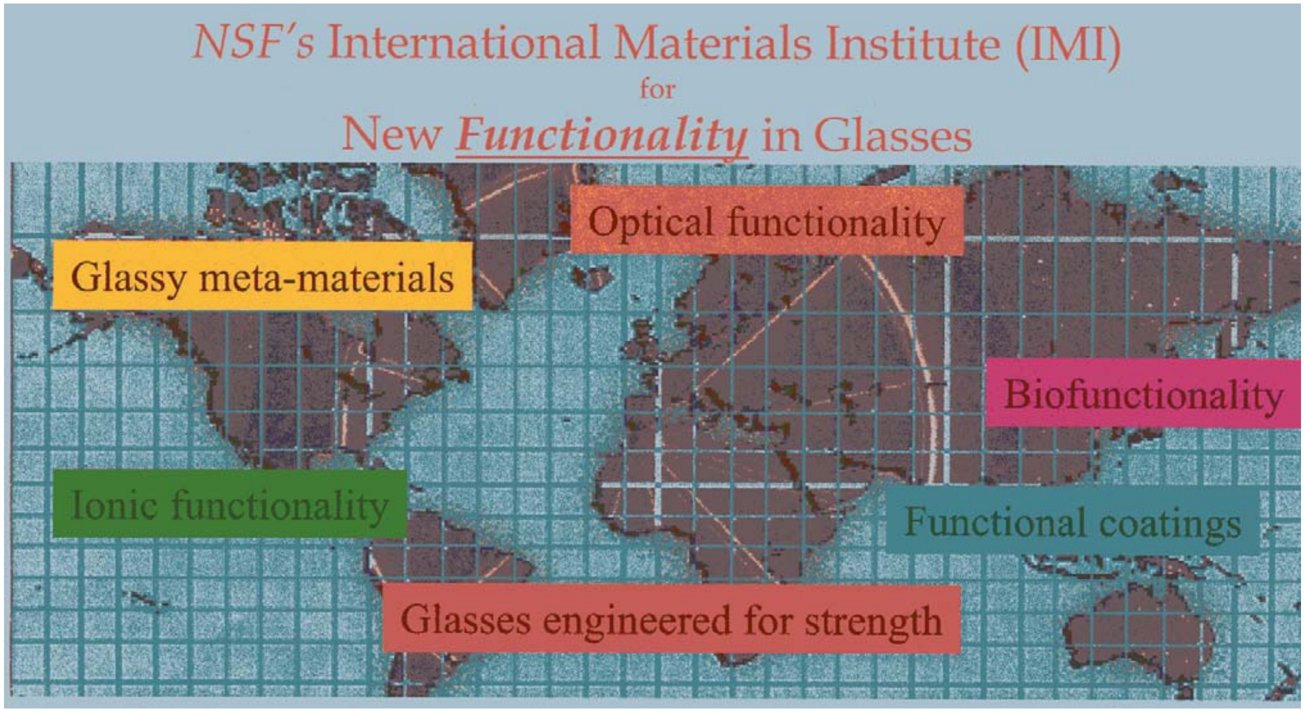


Goals of IMI-NFG:

- **International Colaboration with Research Trust on 6 new Functionalities**
- **Multimedia Glass Education delivered across the boundaries**
- **Outreach/Networking**

Glass Lecture Series: prepared for and produced by the
International Material Institute for New Functionality in Glass
An NSF sponsored program – material herein not for sale
Available at www.lehigh.edu/imi

Questions

- **What is lithography? What is glass?**
- **Can glass be photosensitive?**
- **Can glass be selectively etched/featured? If yes, how and what is the resolution limit?**
- **Can a glass be applied in lithographic process and vice versa can lithography be applied to structure glasses?**

Lithography – what does it mean?

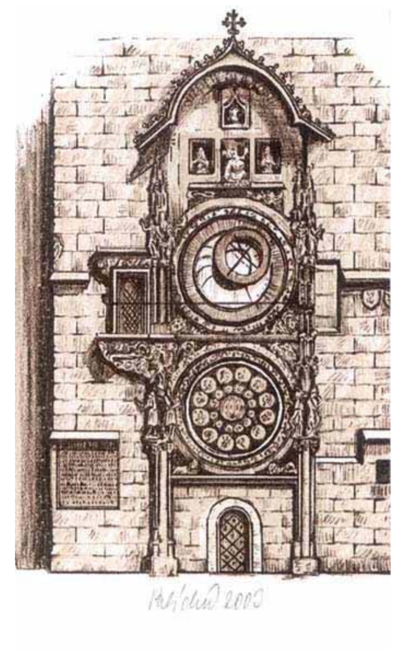
in ancient Greek: lithos = stones graphia = to write

discovered by Alois Senefelder (Prague, Bohemia currently Czech Republic) in 1796

- **oil-based image painted on the smooth surface of limestone**

- **nitric acid (HNO_3) emulsified with gum arabic burns the image only where surface unpainted and gum arabic sticks to the resulting etched area.**

- **printing – water adheres to the gum arabic surface and avoids the oily parts, oily ink used for printing is doing exactly opposite, positive image is transferred on paper**



http://sweb.cz/galerie.litografie/

„Technical“ understanding of term lithography these days:
formation of 3-D relief images in a film on the substrate with the aim of transferring them subsequently to the substrate

Microlithography **– pattering method which allows features smaller than 10 µm to be fabricated**

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

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

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

What lithography involves?

- an exposure (irradiation) source

- a mask and/or computer controled scan of suitable beam
  across resist-coated substrate

- a resist itself

- 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 fabricated

How resists work?

resist – radiation sensitive material, where chemical reactivity of exposed parts is modified relative to unexposed parts

Etchant – agent (solvent, gas) which preferentially etches

the exposed parts → **positive etching**

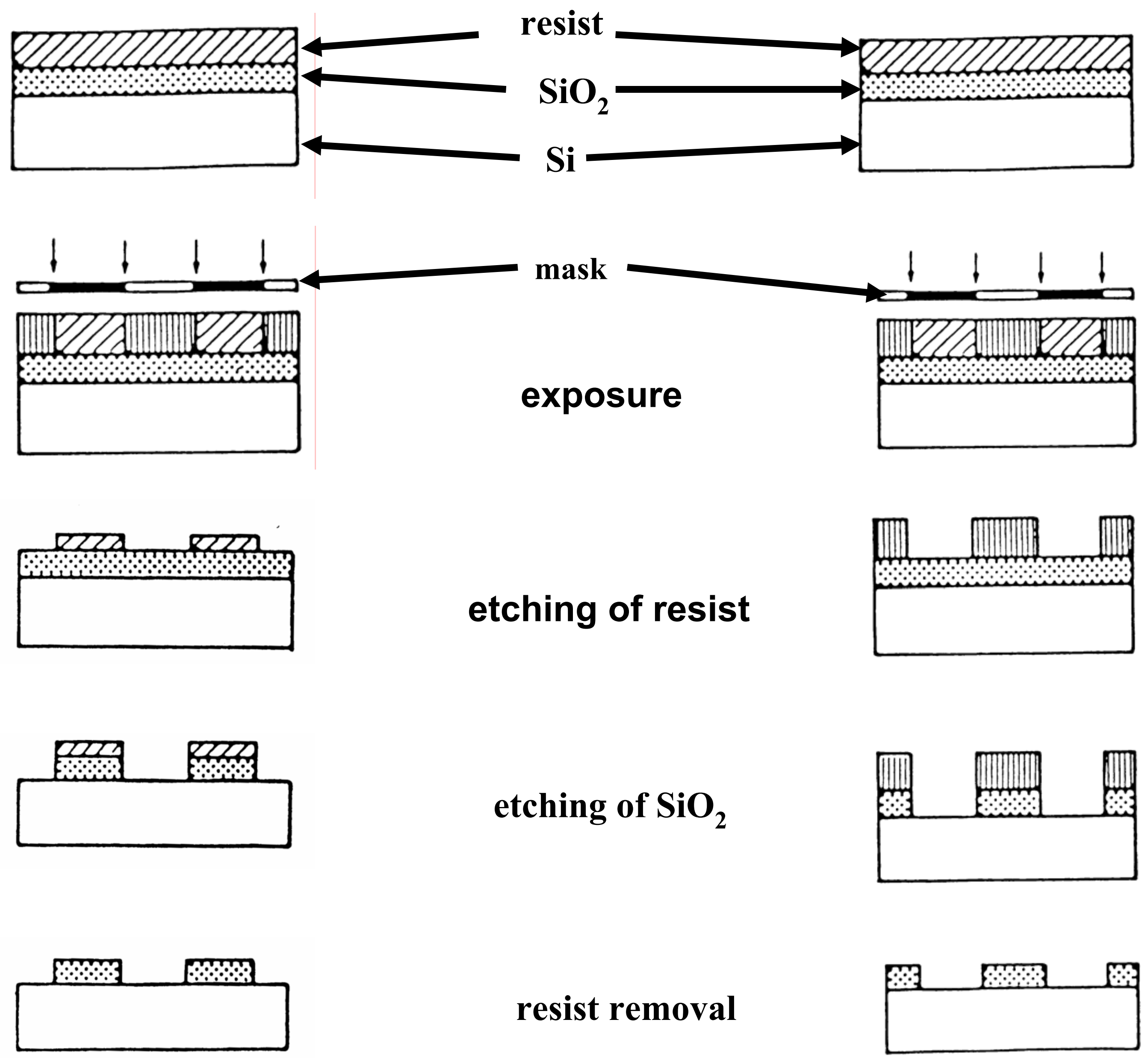
the unexposed parts → **negative etching**

original patterns are thus transferred into the resist

after that substrate is patterned in resist-notcovered regions only

all resist removed from corrugated substrate

positive etching **negative etching**



Most important parameters of any resist

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

Resistent to agents applied for substrate etching

High resolution – nano better

Easy to be deposited – homogenous in properties and thickness

What is glass?

Glass – solid matter which is produced when the viscous molten material cools very rapidly to bellow its glass transition temperature and there is not sufficient time for atoms to form regular crystal lattice

Silica based glasses – most common type of glasses

about 70 % by weight of SiO_2

soda-lime glass (≈ 30 % Na_2O + CaO)

borosilicate glass (≈ 10 % B_20_3)

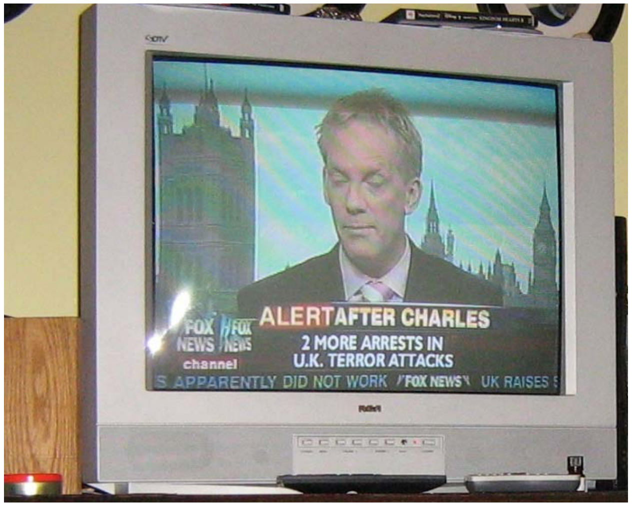
lead crystal (at least 24 % of PbO)

brittle, under compression can withstand a great force, chemically quit resistant, stable

3D compact structure, strong Si-O bonds

obsidian – natural glass

http://www.galleries.com/minerals/mineralo/obsidian/obsidian.htm

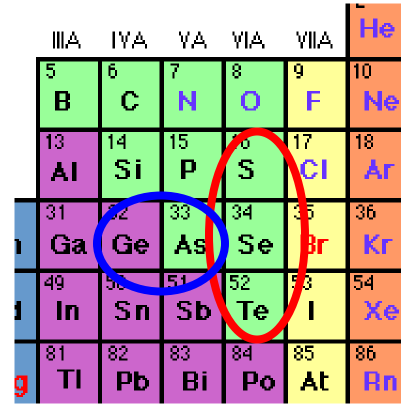


chandelier in Capital, Washington

New York – Trump Tower and Times Square

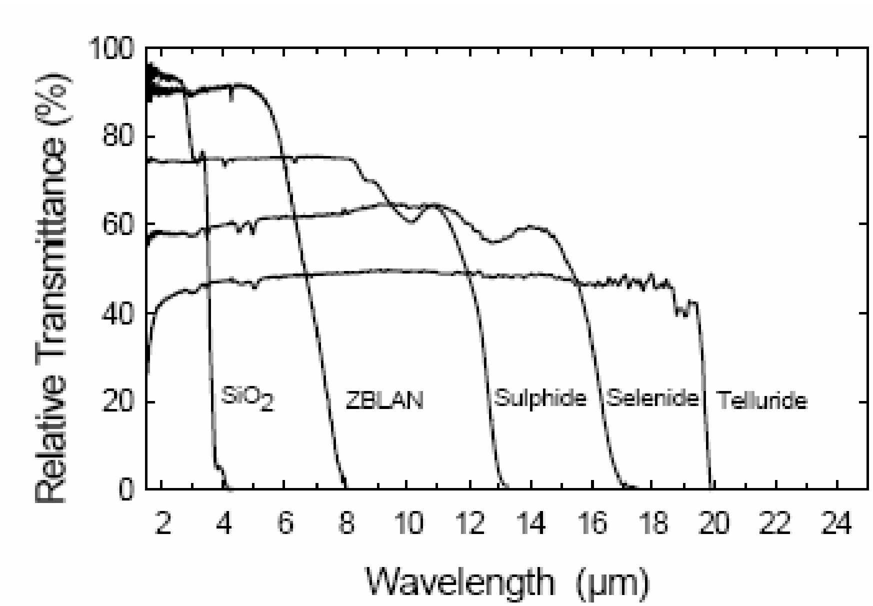
But go back a little bit to science

Chalcogenide glasses - nonoxide glasses

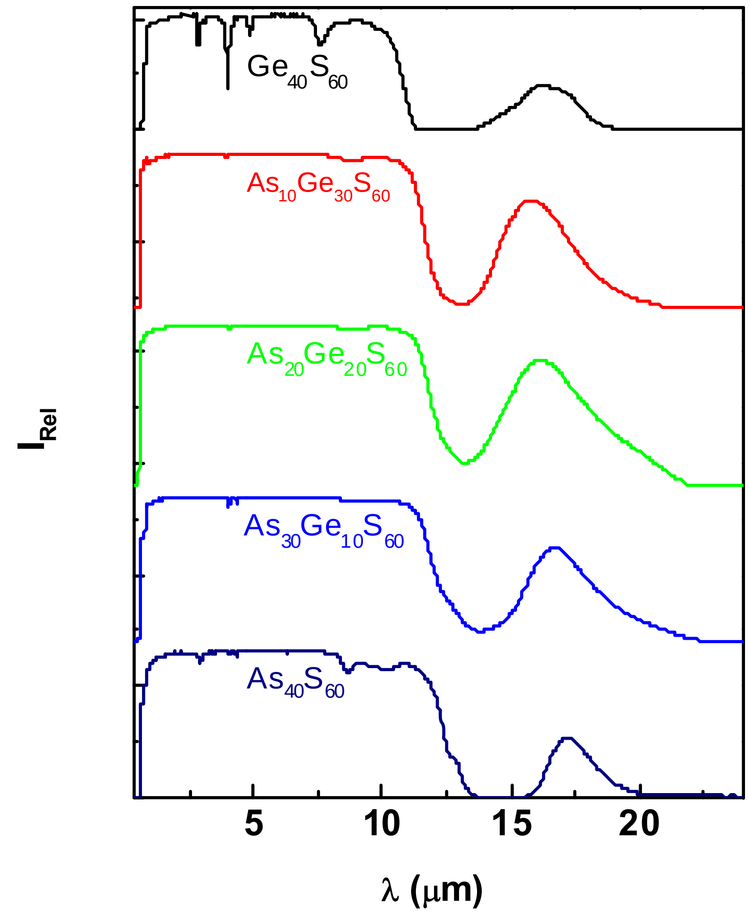


O replaced by S, Se or Te

- **significantly lower T_g than oxide glasses**
- **transmission in IR**
- **high refractive index (≈ 1,8 – 3,2)**
- **!!! sensitive to different radiation!!!**



I. D. Aggarwal, J. S. Sanghera Journal of Optolectronics and Advanced Materials Vol. 4, No. 3, September 2002, p. 665 - 678



R. Ston, M. Vlček, H. Jain: J. of Non-Cryst. Solids 326&327 (2003) 220 – 225

Tailoring the properties

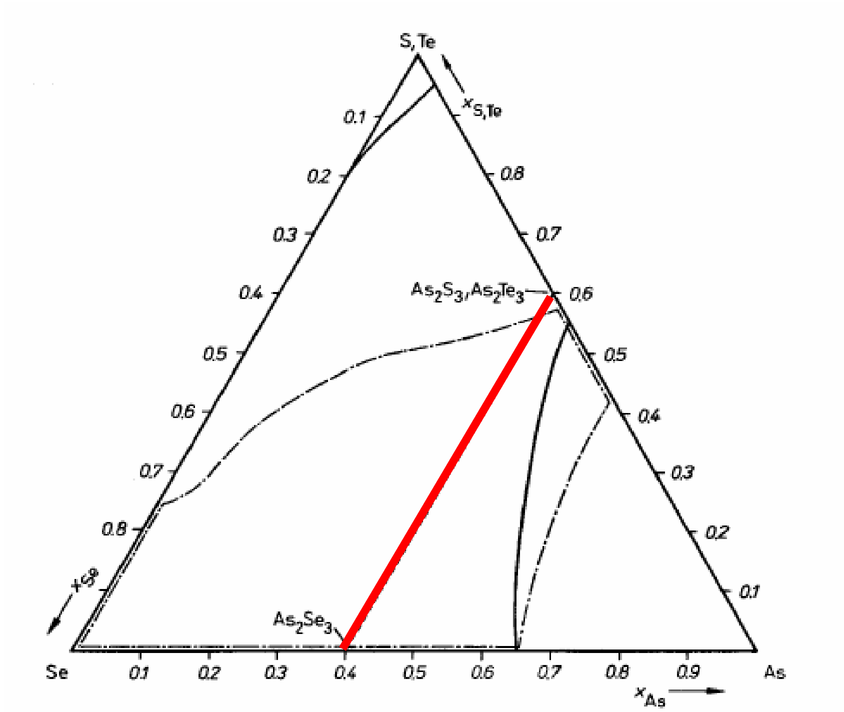


Fig. 3.47. Ranges of glass formation in the As–S–Se (——) and As–Se–Te systems (–·–·).

Adopted from A. Feltz:Amorphous Inorganic Materials and Glasses, VCH, 1993, Berlin, Germany

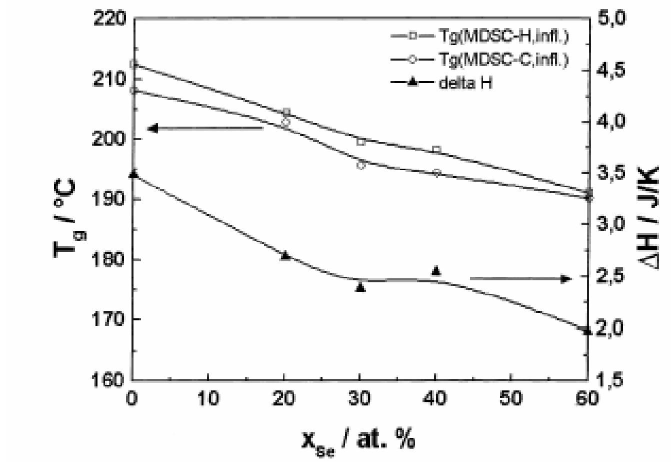
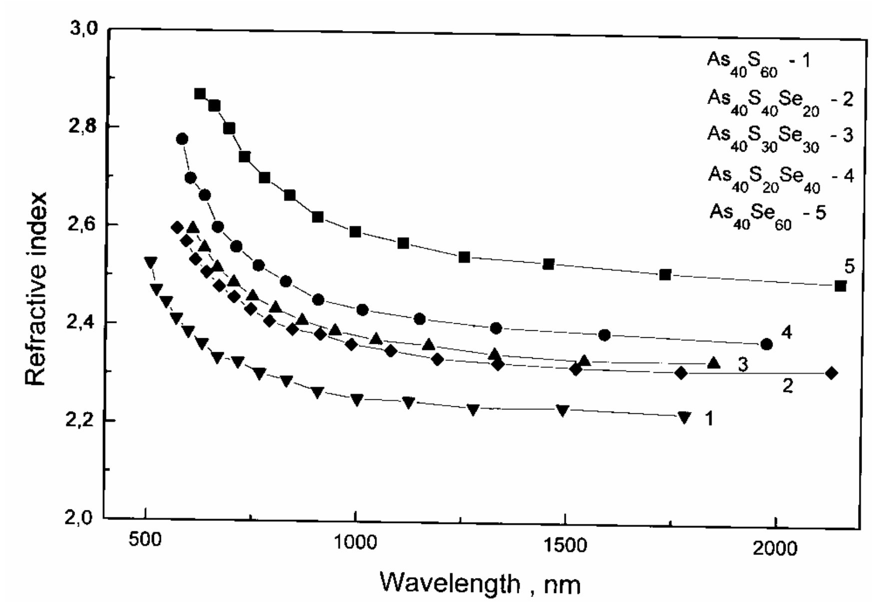


Fig. 1. Glass transition temperature, T_g, and relaxation enthalpy ΔH vs composition. Lines are drawn as guides for the eye.

M. Vlcek, A.V. Stronski, A. Sklenar, T. Wagner, S.O. Kasap Journal of Non-Crystalline Solids 266-269 (2000) 964-968



M.Vlček, A.V. Stronski, A. Sklenář, T. Wagner, S.O. Kasap: Journal Non-Cryst. Solids 266-269 (2000) 964-968

Tailoring the properties

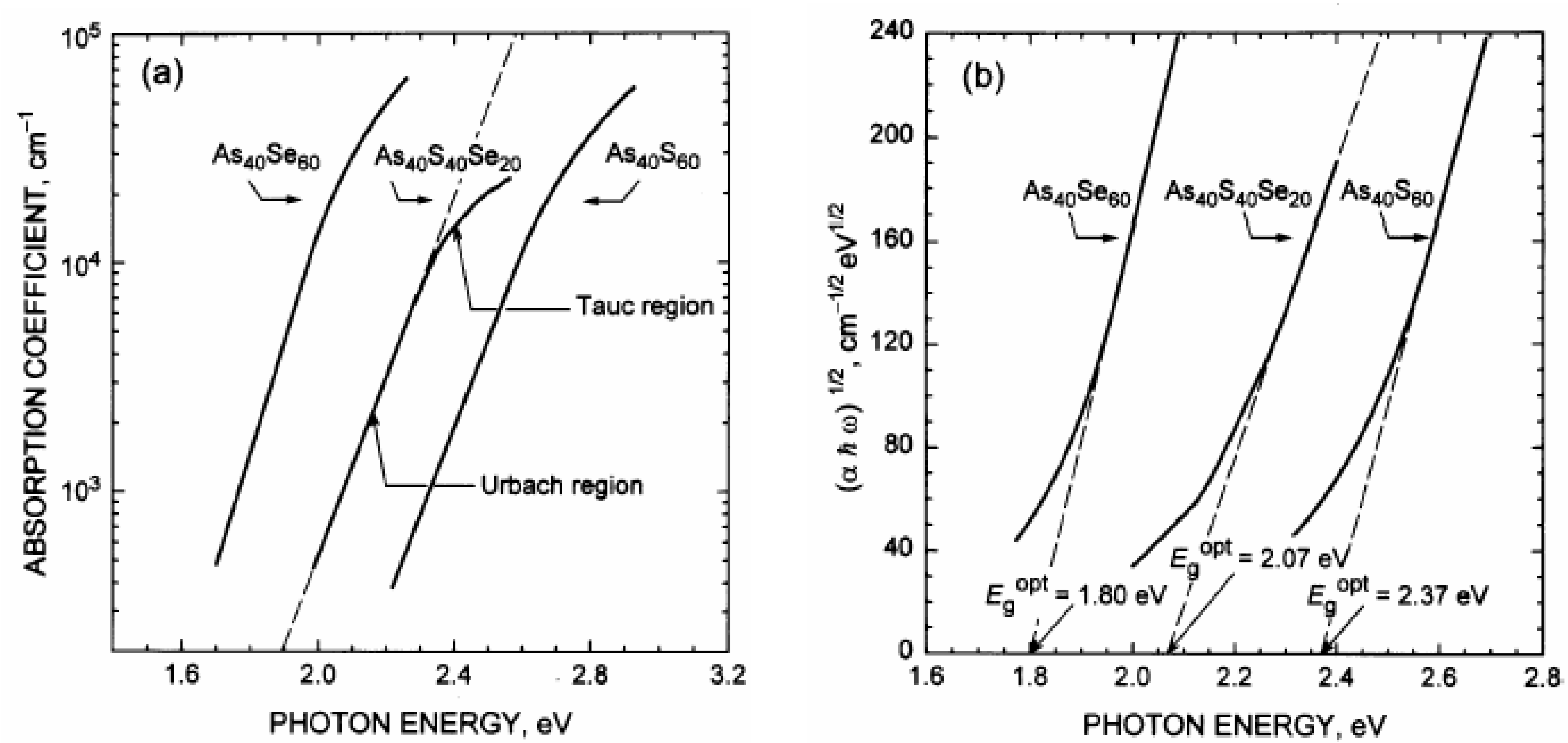


Fig. 5. a Absorption coefficient as a function of the photon energy for the three chalcogenide glassy compositions, $As_{40}S_{40}Se_{20}$ (this work), $As_{40}S_{60}$ and $As_{40}Se_{60}$. b Determination of the optical gap, E_g^{opt} , in terms of the Tauc law

E. Marquez, J.M. Gonzales-Leal, R. Prieto-Aleon, M. Vlcek, A. Stronski, T. Wagner, D. Minkov Appl. Phys A 67 (1998) 371

!!! CHG sensitive to different radiation!!!

What is the reason of sensitivity of CHG?

generally – all amorphous materials - thermodynamically metastable

exposure to suitable radiation can cause transformation in their structure or reaction with the environment (O_2, metal, ...) → optical and physico-chemical properties including chemical resistance are influenced

Classification of 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

exposure with suitable radiation can change optical properties (T, R, n, α ...)

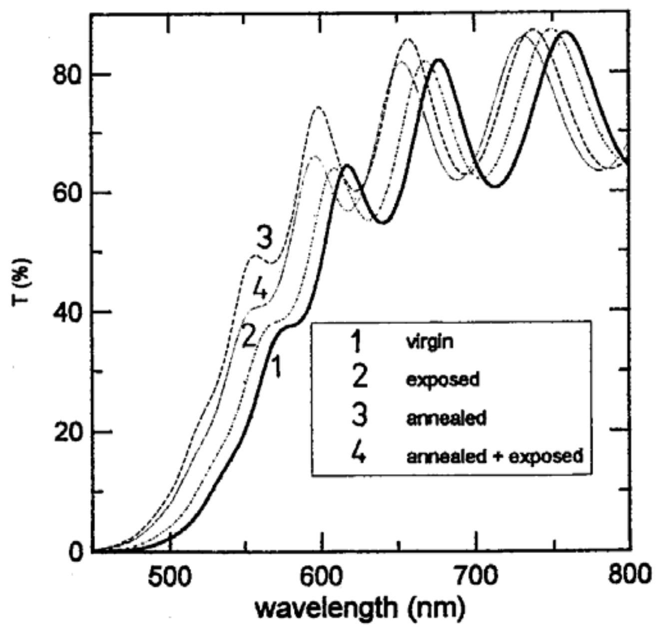
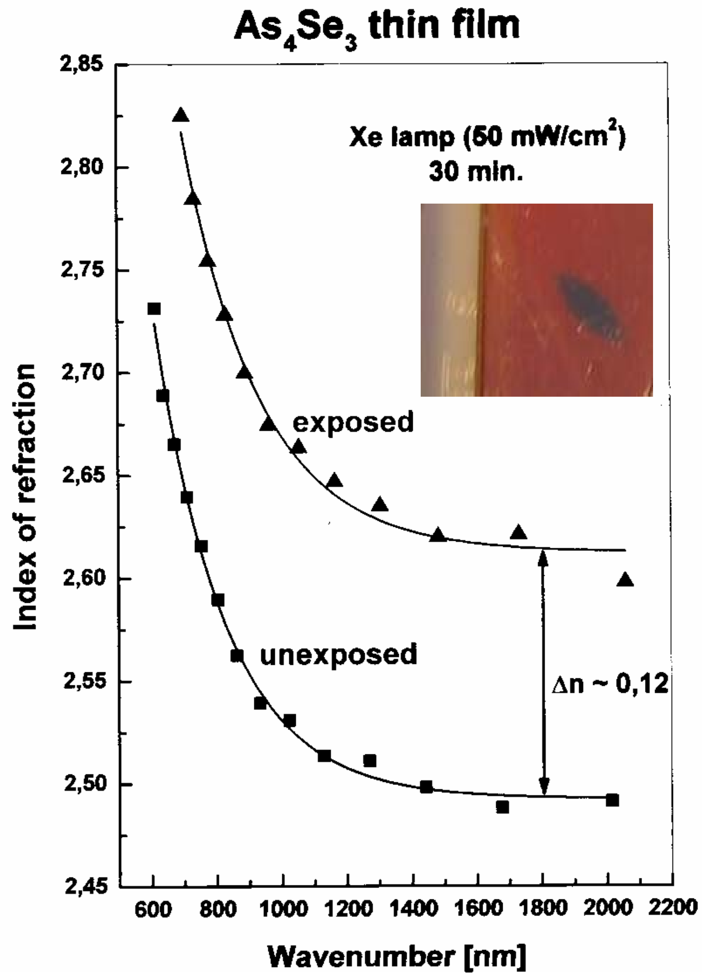


Fig. 1. Spectral dependence of optical transmissivity of $Ge_{30}Sb_{10}S_{60}$ thin film.



M. Vlček, C. Raptis, T. Wagner, A. Vidourek, M. Frumar, I.P. Kotsalas, D. Papadimitriou: Journal Non-Cryst Solids192-193 (1995) 669-673

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 –ray....

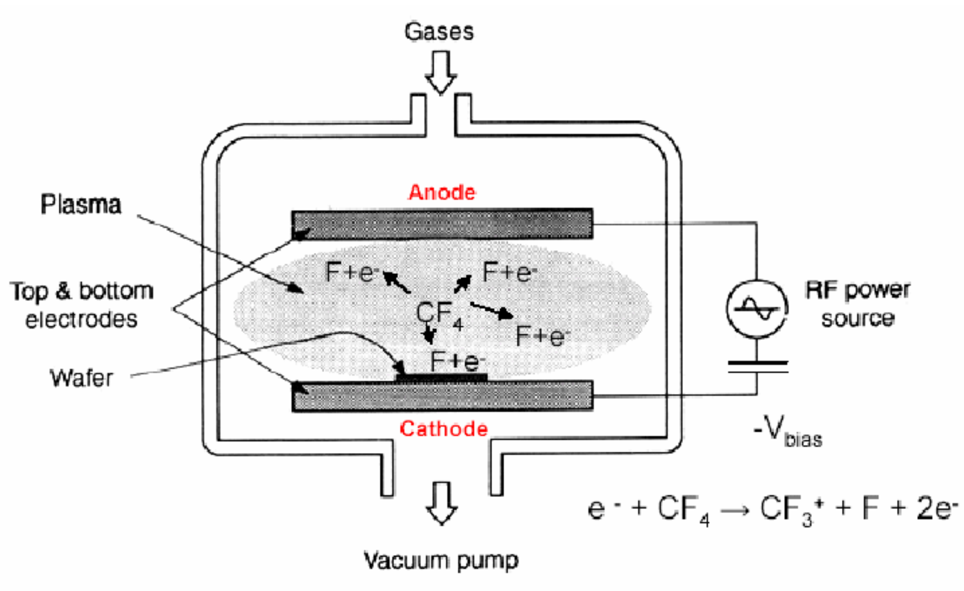
both dry and wet etching can be applied

Wet etching – all photoinduced processes can be applied

Dry etching – usually photo-dissolution of certain metals is applied

DRY ETCHING

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



harsh conditions in plasma requires hard photoresist ! including:

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

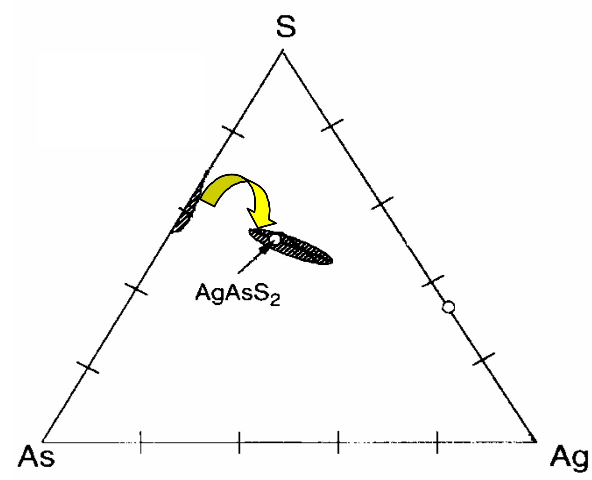
www2.ece.jhu.edu/faculty/andreou/495/2003/LectureNotes/DryEtching.pdf

Certain metals usually added to CHG photoresist – Why?

combine <u>photostructural and compositional changes</u> from photodiffusion of metal (mainly Ag) in ChG is the solution !!!

• *High contrast of resist pattering wanted*
Ag diffuses transversally only, no lateral diffusion

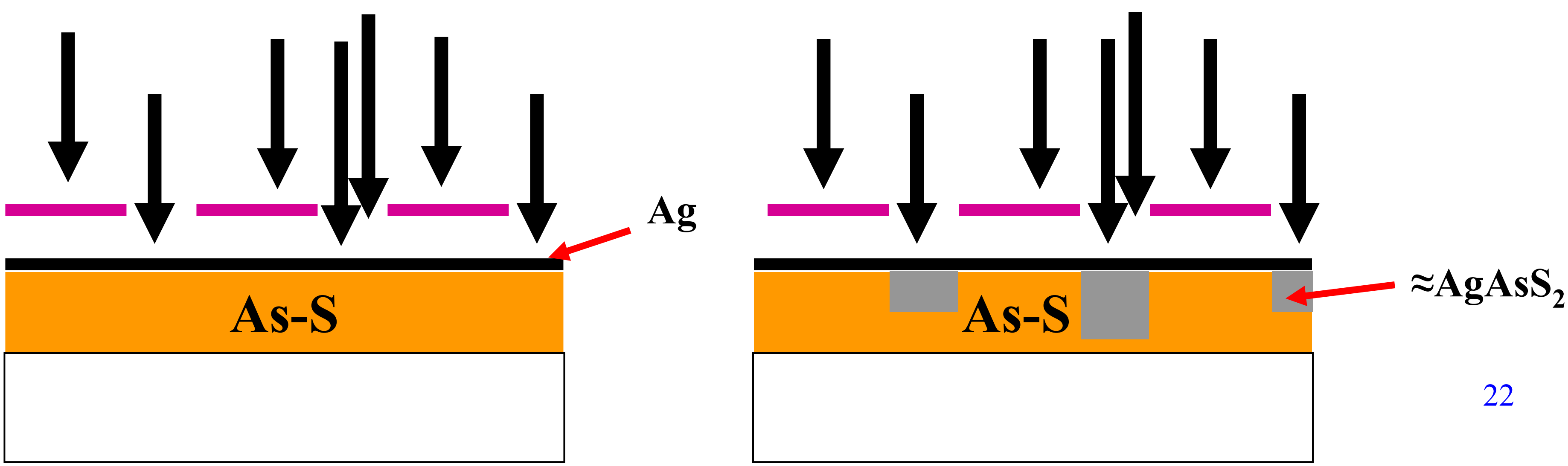
• *resistent to plasma etching gas*
• **resistance increases due to formation ternary Ag-As-S glass but in exposed parts only**



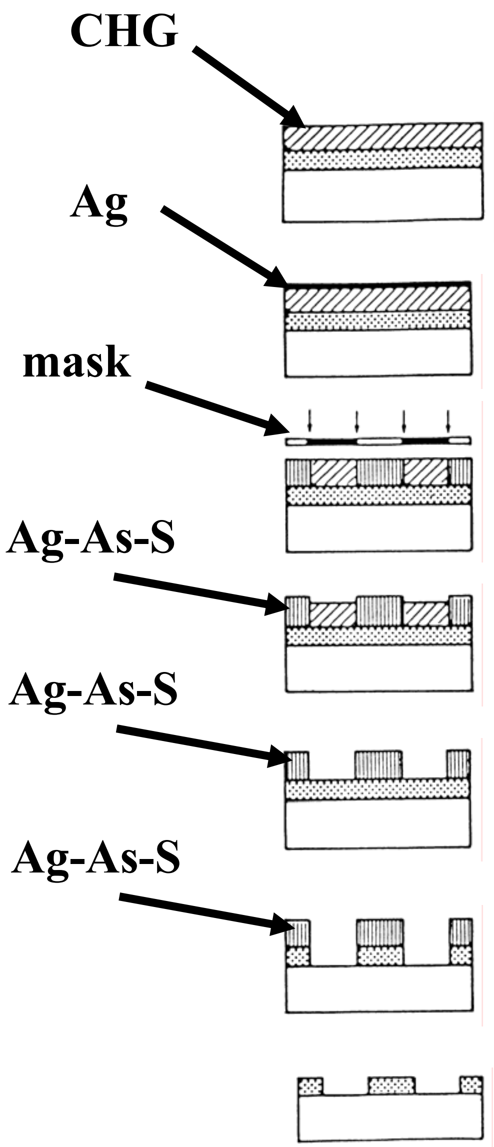
2 glass forming regions

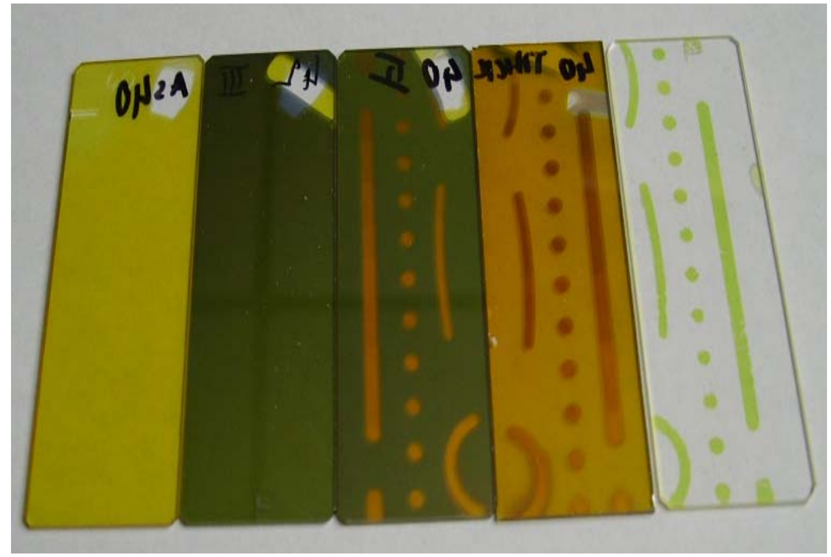
Ag diffuses into As-S step like
- depth of diffusion - function of exposure dose

Drawbacks – two more steps:
- **deposition of Ag**
- **removal of excess Ag from unexposed**



All Dry Process or combined process





- deposition of As-S
- deposition of Ag
- exposure (vertical transfer of Ag into As-S)
- removal of excess Ag from unexposed parts by dry/wet etching
- dry/wet etching of As-S
- dry/wet etching of substrate
- dry/wet removal of Ag-As-S layer from exposed parts

bilayer photoresist Ag + As (and/or Ge) based chalcogenide glass exhibit excellent resolution, high contrast and good resistance to dry etching by CF_4 (+ O_2)

Materials	Etch Gases	Etch Products
Si, SiO2, Si3N4	CF4, SF6, NF3	SiF4
Si	Cl2, CCl2F2	SiCl2, SiCl4
Al	BCl3, CCL4, SiCl4, Cl2	AlCl3, Al2Cl6
Organics	O2, O2 + CF4	CO, CO2, H2O, HF
other: (W, Ta, Mo..)	CF4	WF6,..

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

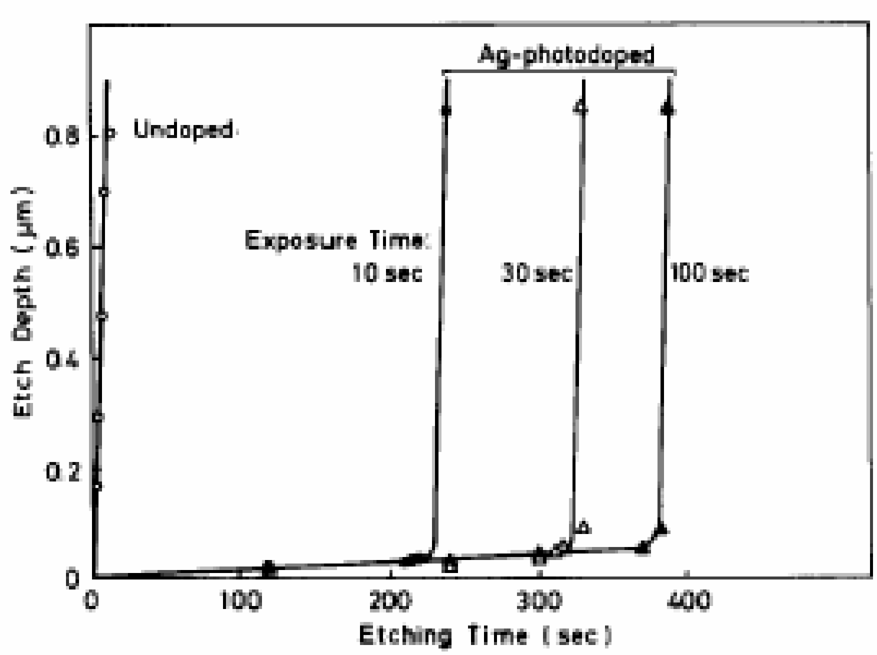


FIG. 1. Plasma etching characteristics of undoped and Ag-photodoped $Se_{75}Ge_{25}$ film.

A. Yoshikawa Appl.Phys.Lett. 36(1) 107

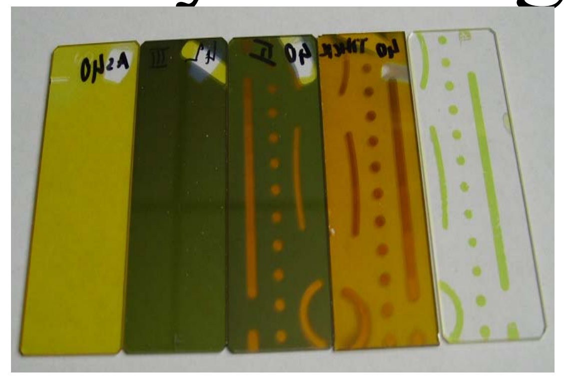
Sensitization - evaporation of Ag
200 W Hg lamp, 60 mW/cm^2
excess Ag removed in HNO_3-HCl-H_2O
0.5 Torr CF_4 gas, 100 W rf power

etching rates:
undoped 55 nm/sec
Ag photodoped 0.15 nm/sec

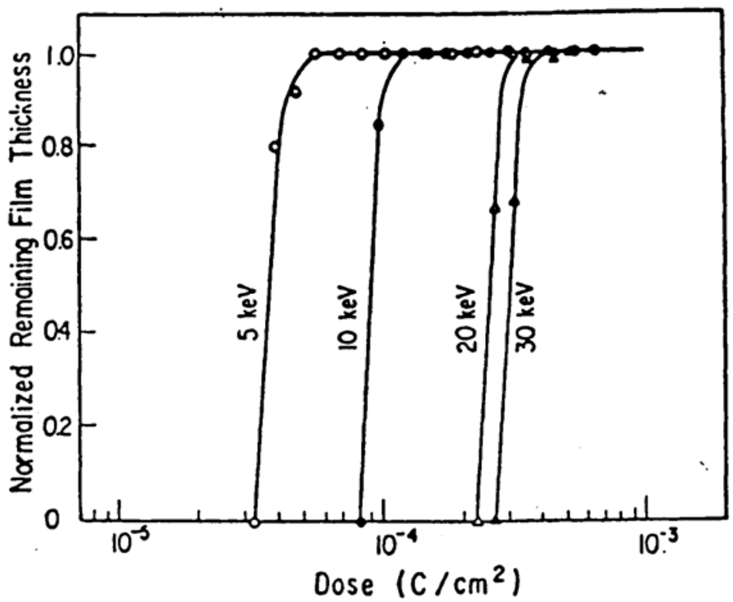
Patterning Options for dry etching

Different sources !!!

UV or visible light



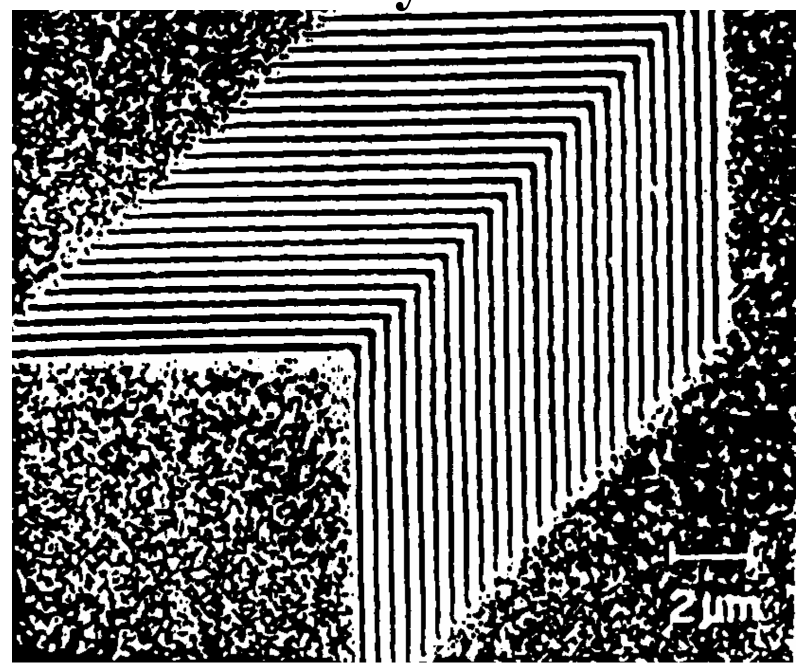
e - beam



Electron-beam exposure characteristics of Ag-$Se_{85}Ge_{15}$ system. Remaining film thickness is normalized in the terms of the initial 280 nm thickness

Y.Mizushima and A.Yoshikawa „Photoprocessing and lithographic applications", In: Amorph. Semicond. , Technolgies & Devices : Tokyo e.a. Amsterdam, 277-295, (1982).

X – ray beam

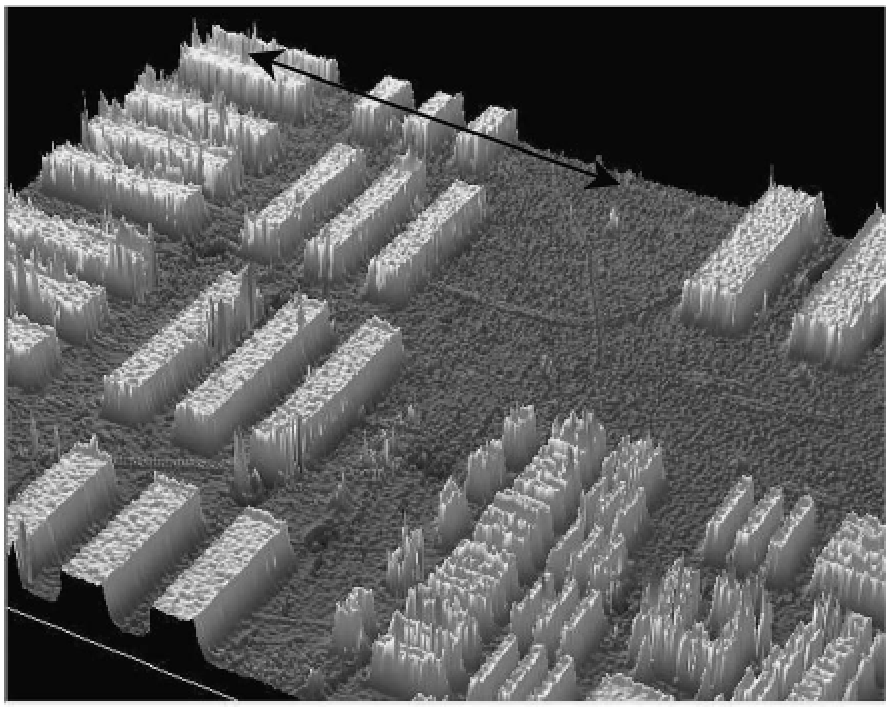


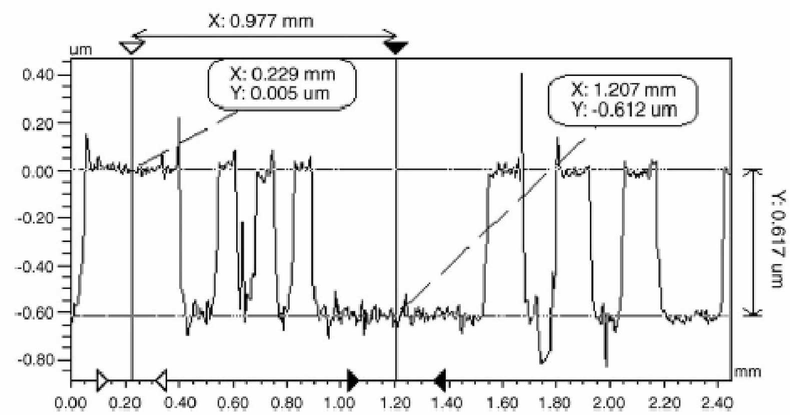
X-ray lithography utilizing inorganic resist - 0.2 µm line/space pattern

K.Saito,Y.Utsugi, and A.Yoshikawa „X-ray lithography with Ag-Se/Ge-Se inorganic resist using synchrotron radiation", J.Appl.Phys., 63 (2), 565-567, (1988).

Dry etching

Negative dry etching of Ag-As_2S_3 bilayer resist by CF_4/O_2

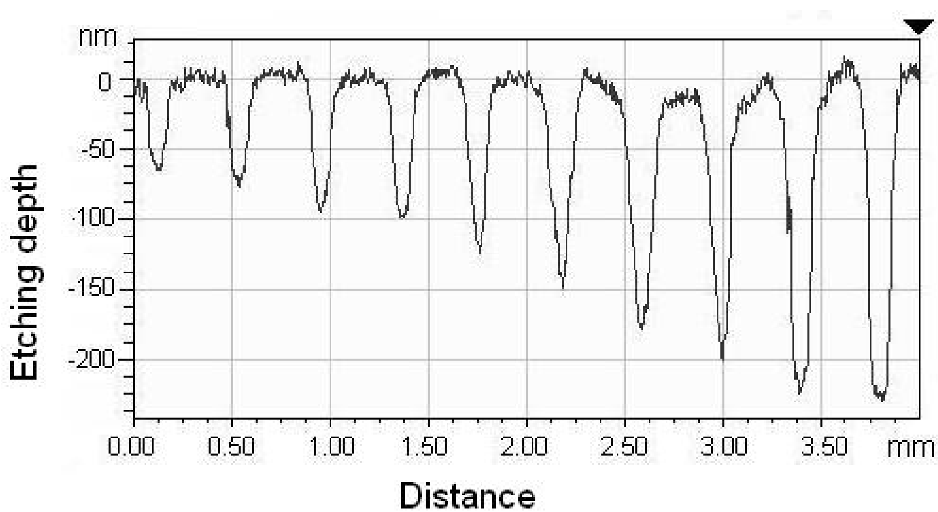




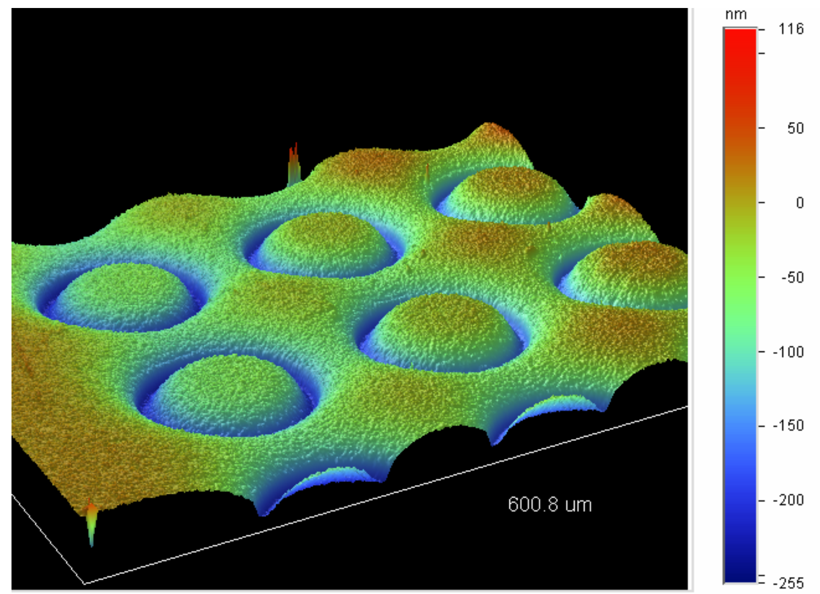
A. Kovalskiy, M. Vlcek, H. Jain, A. Fiserova, C.M. Waits, M. Dubey Development of chalcogenide glass photoresists for gray scale lithography Journal of Non-Crystalline Solids 352 (2006) 589–594

Dry etching of shaped structures

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



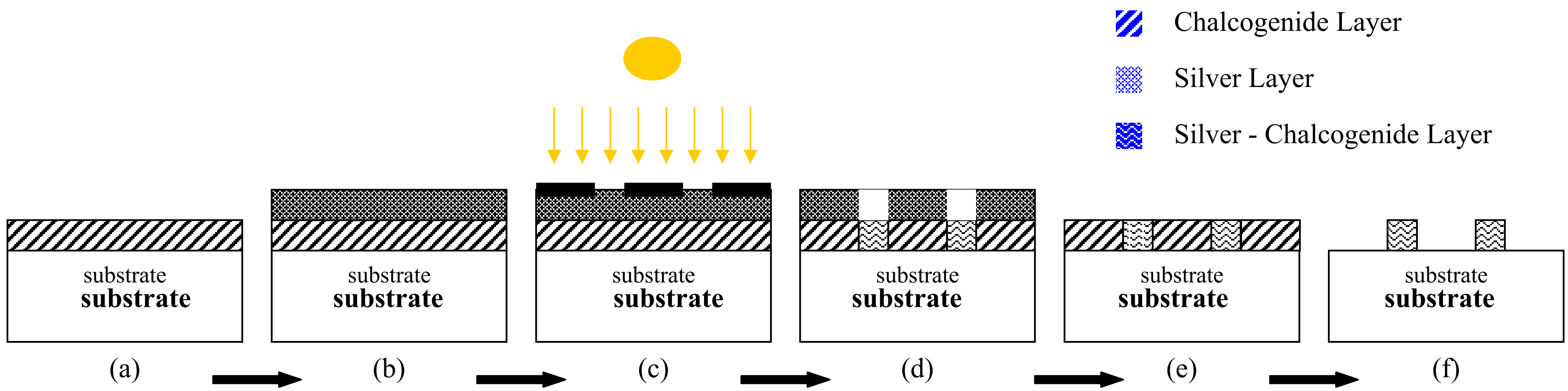
Profilogram demonstrating the change of etching depth with gradual variation of transparency of mask fragments.

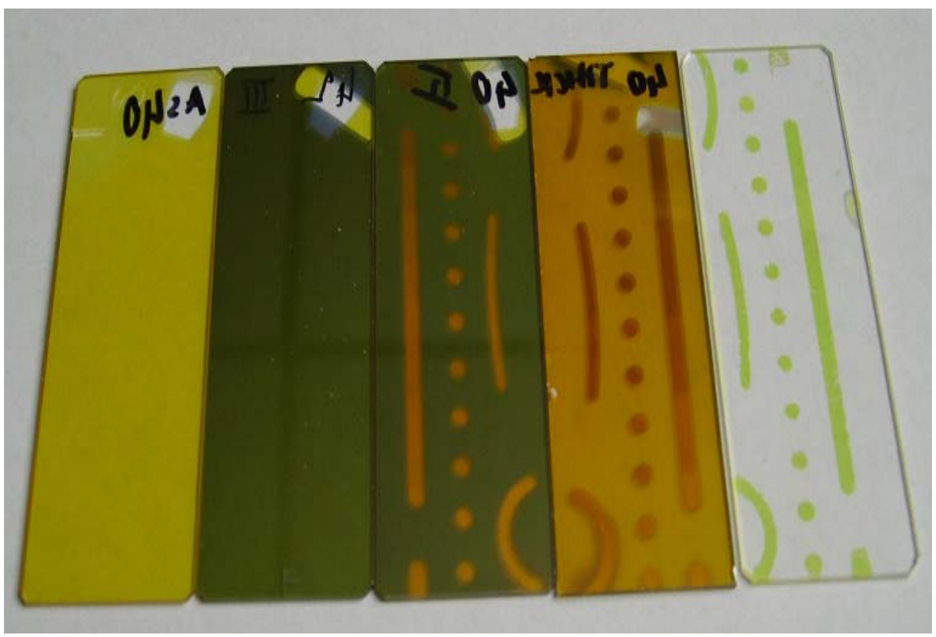


Optical Profiler image demonstrating the possibility of smooth shaping with lens-like mask by photoinduced Ag diffusion into As_2S_3 film with following dry etching (reverse image, depth of etching 200 nm). CF_4 as the etchant gas, with pressure of 100 mTorr, an electrode power of 110 W, CF_4 flow rate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

Photodoping Phenomenon for Enhanced Selectivity





a b d e f

(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

Photodiffusion enhanced lithography – when to use it???

hard resists applications

Bilayer photoresist ⇒ more complicated technology

BUT

higher sensitivity and selectivity for both, wet and dry etching

combine photostructural and compositional changes from photodiffusion of metal (mainly Ag) in ChG

Dry etching of pure CHG possible too

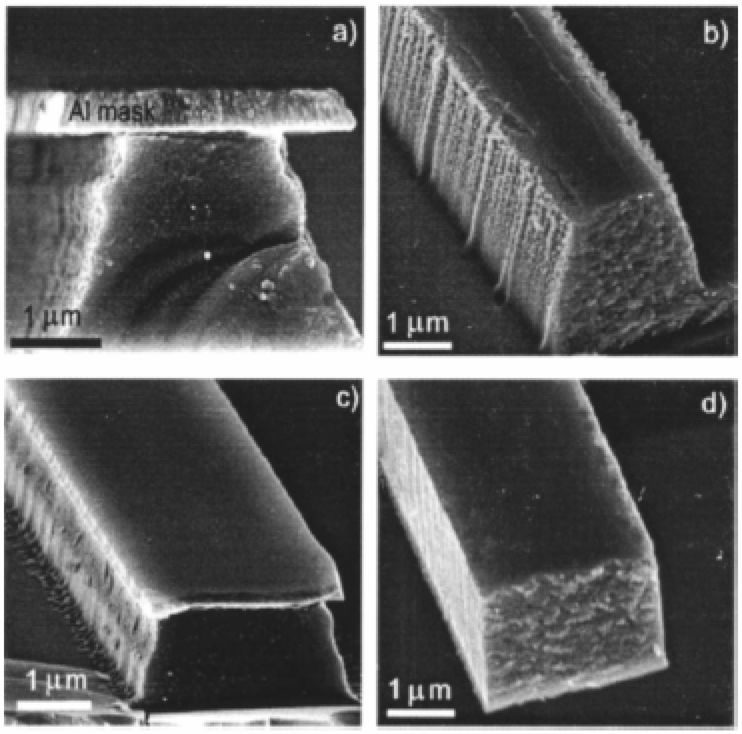


FIG. 10. Micrographs of the As_2S_3 waveguides obtained using different etching condition: (a) $O_2/CF_4=1/1$, $P=600$ W, and $V_b=-120$ V; (b) $O_2/CF_4=7/3$, $P=1000$ W, and $V_b=-120$ V; (c) $O_2/CF_4=7/3$, $P=600$ W, and $V_b=-50$ V; (d) $O_2/CF_4=7/3$, $P=600$ W, and $V_b=-120$ V. The processing pressure was 10 mTorr for all samples.

TABLE I. Etch rate of As_2S_3 films floated in different plasma with a power of 600 W.

Sample	Gas flow (sccm)	Etch time (min)	Etch rate (nm/min)
1	$O_2=70$	10	0
2	Ar=70	10	20
3	$CF_4=90$	2	1500
4	CF_4/Ar=30/70	2	210
5	$CF_4/O_2=30/70$	2	130
6[a]	$CF_4/O_2=30/70$	2	20
7[b]	$CF_4/O_2=30/70$	2	100

[a]The sample surface was preoxidized in an O_2-plasma.
[b]The sample was positive biased with dc 60 V.

diluted CF_4 must be applied

W. Li at al. J. Vac. Sci. Technol. A 23 (6) (2005) 1626 - 1632

WET ETCHING

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)

Parameters influencing selectivity of wet etching

Sample composition, method and conditions of thin films preparation

Prehistory of sample – virgin vs annealed

Exposure conditions (I, λ, T, τ, environment...)

Etching conditions (composition of etching bath, pH, temperature..)

Method and conditions of thin films preparation

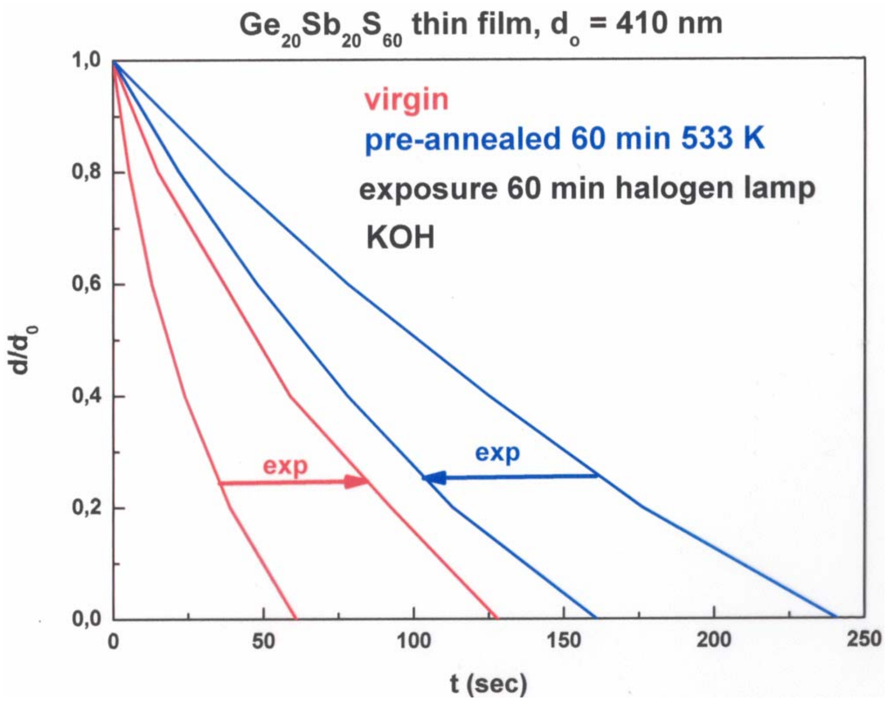
all amorphous materials - thermodynamically metastable
<u>thin layers farther from the equilibrium than bulk</u>

• vacuum evaporation
fast condensation of fragments that exist only in vapour state – final structure influnced by v_{dep}, p, substrate temperature, rotation of substrate..

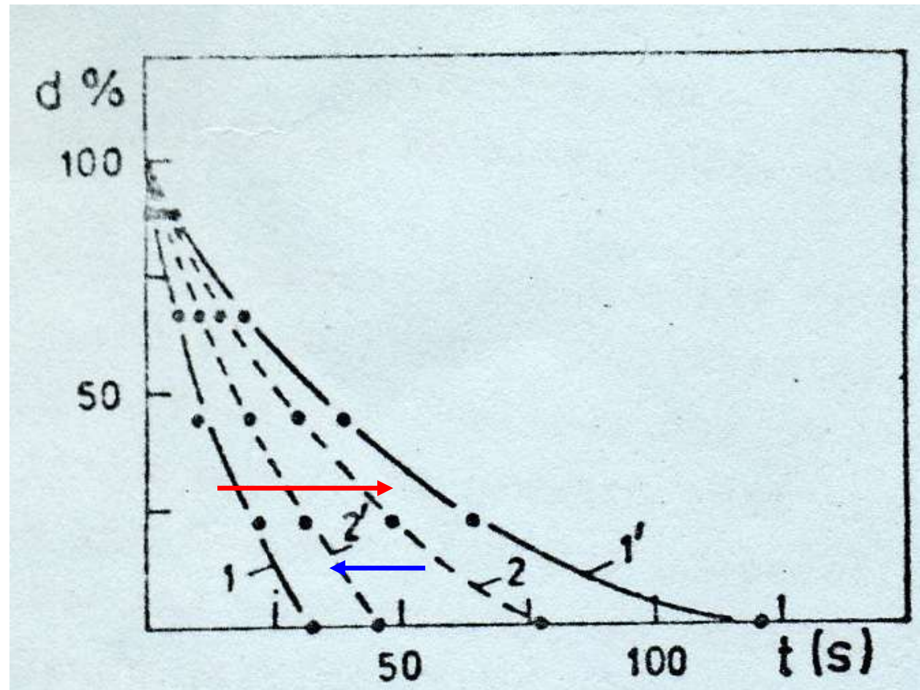
• PE - CVD
deposited at low temperature, H_2 is incorporated in samples prepared by PE – CVD

• spin coating
deposited at low temperature, residual amount of the dissolver is „captured“ in the structure

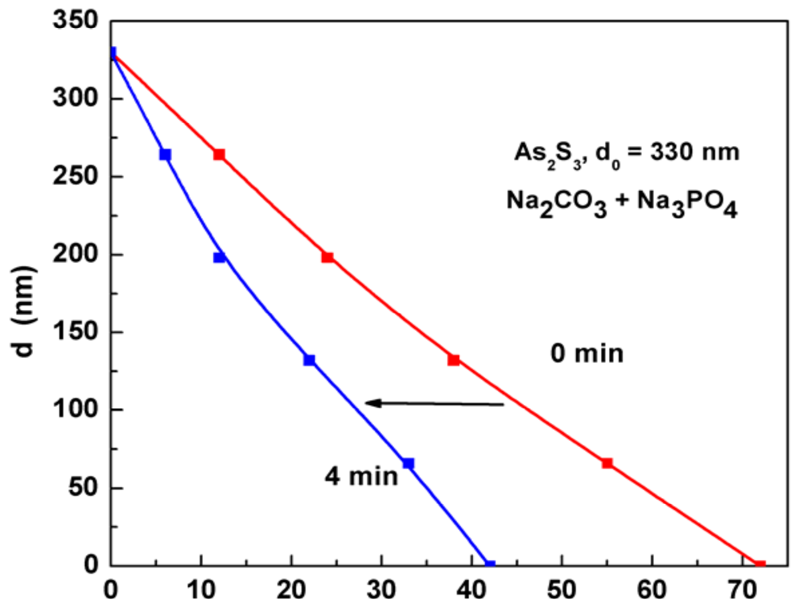
Prehistory of the sample virgin vs annealed



M. Vlcek Ph.D. Thesis



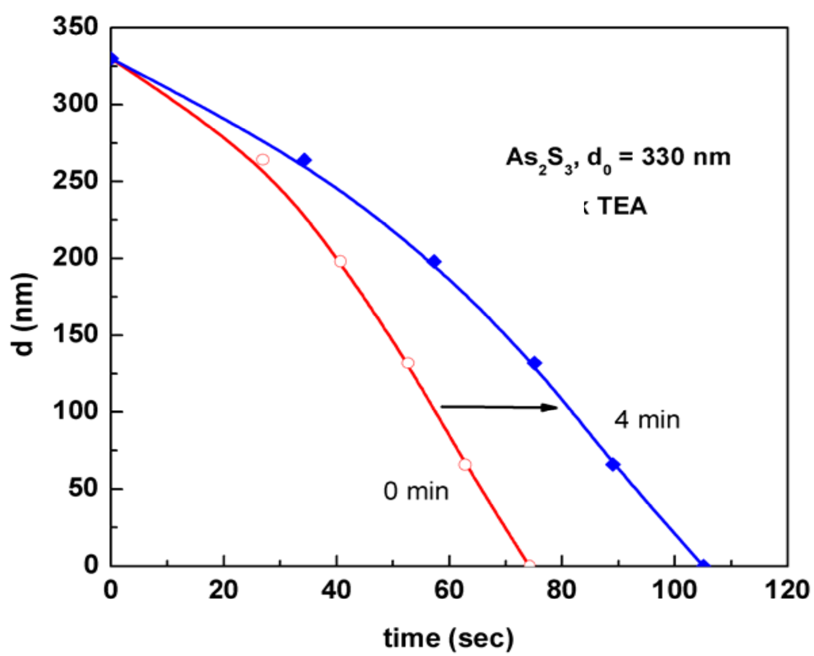
$Ge_{30}S_{60}In_{10}$, 1,2 – non-irradiated, 1´,2´- irradiated, 2,2´- previously annealed at 430 K
Z.G. Ivanova: Proc. of Int. Conf. Amorphous Semiconductors, Gabrovo, 1984, Vol. 2, p. 268



Etching bath

Aqueous base

Positive etching



Organic amine base

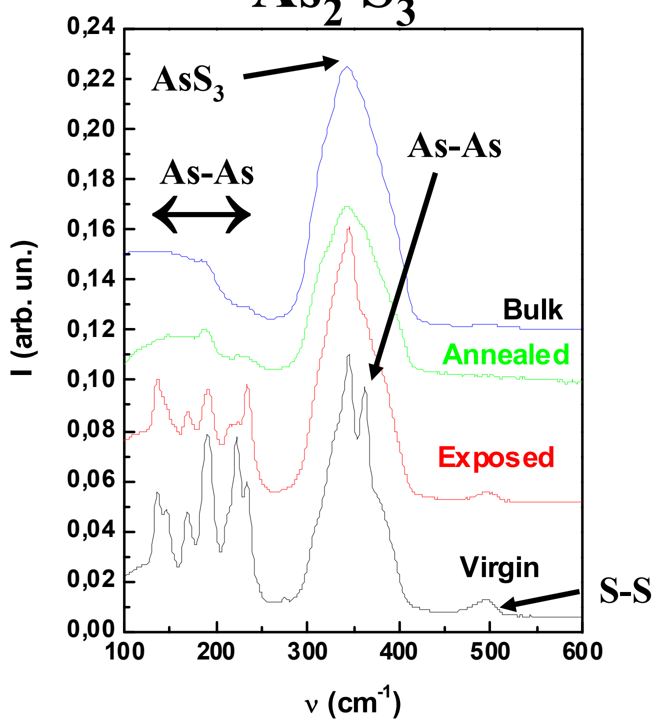
Negative etching

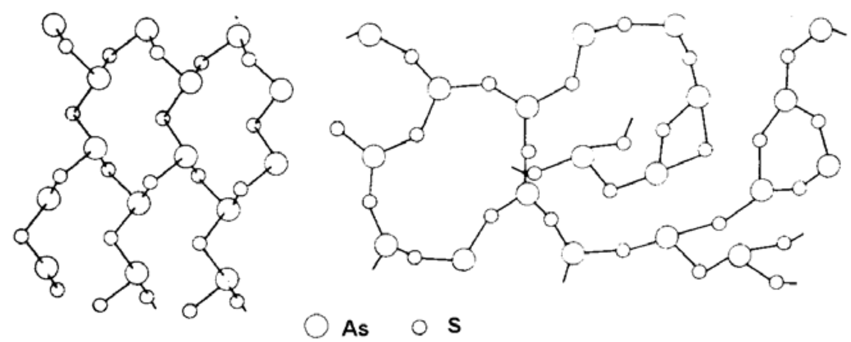
What is the fundamental cause of sensitivity and changes in chemical resistance?

Different CHG composition and different sources of radiation - different reason, let us discuss only most common case – band gap exposure photosensitivity of as-evaporated As-S thin films

vacuum evaporation -fast condensation of fragments that exist only in vapour state

$As_2\ S_3$

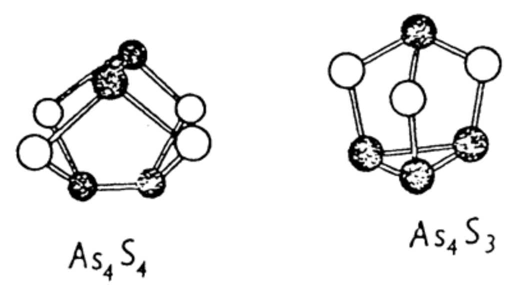


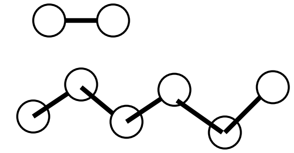


crystal **amorphous**

AsS_3 pyramids

Felc A : Amorfnye i stekloobraznye tvjordye neorganičeskie tela "MIR" Moskva (1986) 283





As_2S_3 orpiment **As_4S_4 realgar** **cages** **S_n chains**

What is the fundamental cause of sensitivity and changes in chemical resistance?

vacuum evaporation - fast condensation of fragments that exist only in vapour state

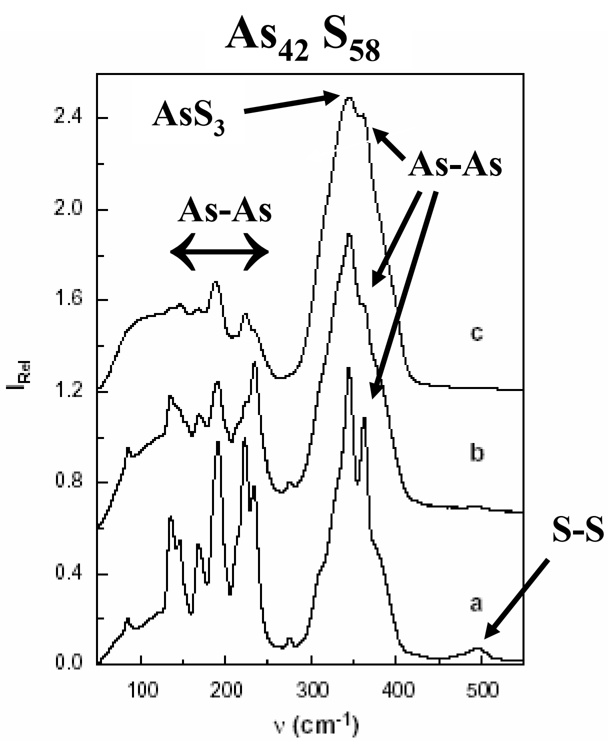


Fig. 1. Raman spectra of $As_{42}S_{58}$ thin layers as-evaporated (a) and exposed (b) and of bulk sample (c). Exposure time 30 min, halogen lamp with 20 mW/cm^2.

photoinduced changes of homopolar bonds concentration

$$\text{As-As} + \text{S-S} \xrightarrow{h\nu} 2\ \text{As-S}$$

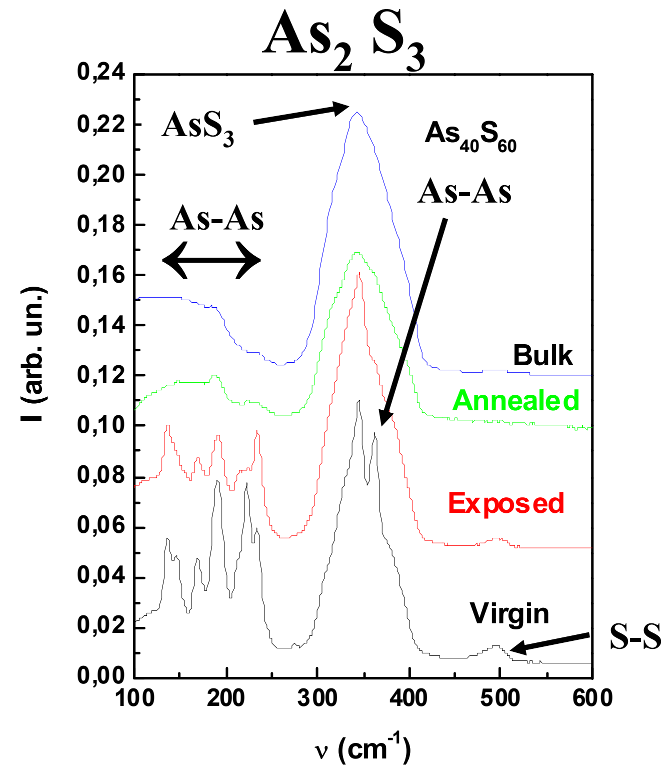
In general:

aqueous base solvents - positive etching

non-aqueous solvents – negative etching

M. Vlček.,S. Schroeter.,J. Čech, T. Wagner, T. Glaser
J. of Non-Cryst. Solids 326&327 (2003) 515 – 518

Mechanism of selective POSITIVE etching in aqueous solvents



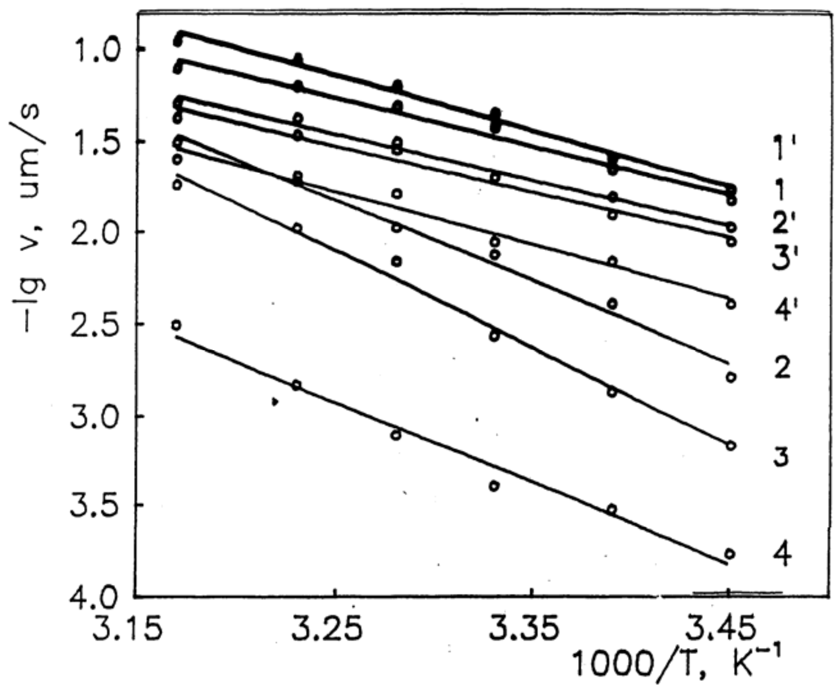
Dissolution of As_2S_3 and As_4S_4 crystals:

$As_2S_3 + 6\ OH^- = AsO_3^{3-} + AsS_3^{3-} + 3\ H_2O$
well soluble

$3\ As_4S_4 + 24\ OH^- = 4\ AsO_3^{3-} + 4\ AsS_3^{3-} + 4\ As + 12\ H_2O$
low dissolution rate due to protective As film; insoluble in solutions with low concentration of OH^-

Glassy samples:
As_4S_4, As_4S_3 fragments present together with S_n fragments in the structure of virgin samples
Exposure or annealing – chemical homogenisation, etching rate increases due to decrease of activation energy of dissolution

Activation energy of dissolution in aqueous K_2CO_3 solution



1,1´ - $As_{28}S_{72}$
2,2´ - $As_{40}S_{60}$
3,3´ - $As_{42}S_{58}$
4,4´ - $As_{45}S_{55}$
X – virgin
X´- exposed by halogen lamp, 14 mW.cm^{-2}

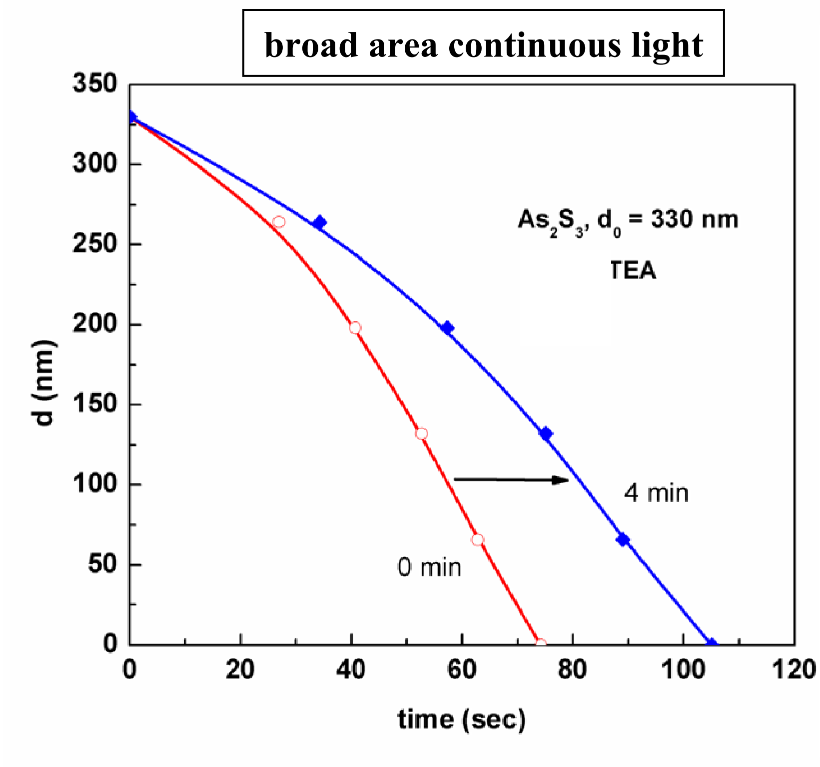
M. Vlček, M. Frumar, M. Kubový, V. Nevšímalová
J. Non-Cryst. Solids, 137-138 (1991) 1035

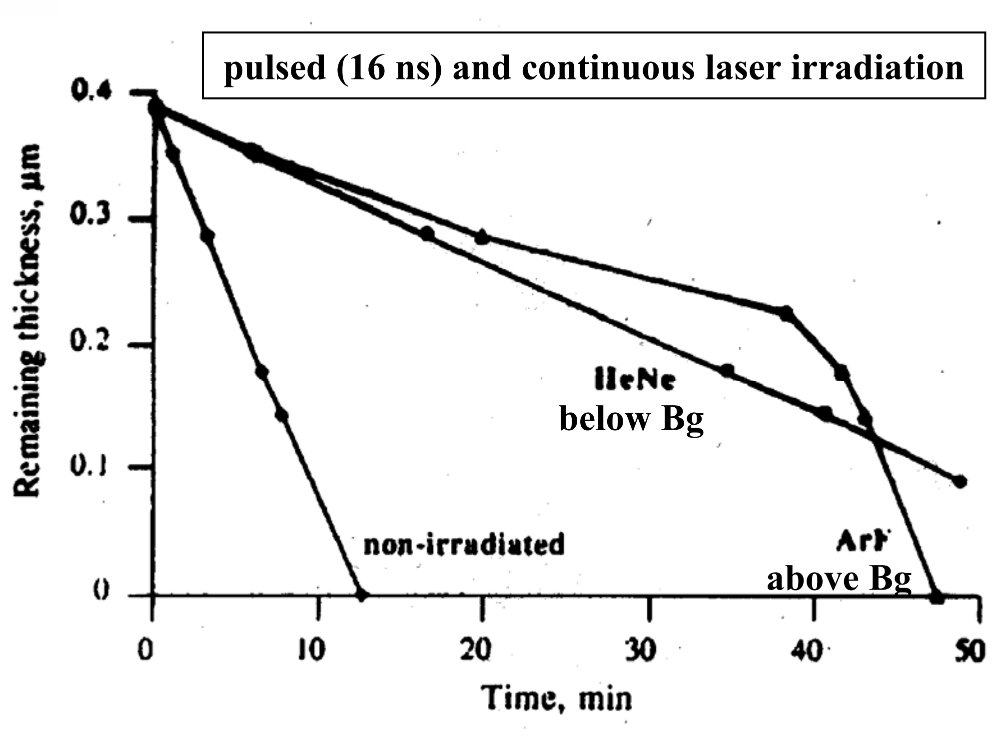
As_xS_{100-x} films

with x ≥ 40: virgin $\Delta E \approx 90$ kJ/mol
exposed $\Delta E \approx 40$-50 kJ/mol
with x < 40: virgin and exposed $\Delta E \approx 45$ kJ/mol

aqueous solvents - positive etching of As rich films

Negative selective etching in non-aqueous base





As_2S_3, triethylamine, halogen lamp

$As_{50}Se_{50}$, ethanolamine, HeNe laser 10 mW, ArF laser (193 nm) 0,5-0,45 mJ single pulses, pulse width 16 ns,
V. Lyubin et al.: J. Vac. Sci. Technol. B 15 (4) (1997) 823

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

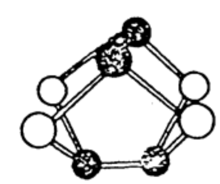
Kinetically controlled process - the ultimate composition of the products is a function of the rate of elementary stages of a process
Amines can promote the cleavage of sulfur rings (or chains)

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

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)



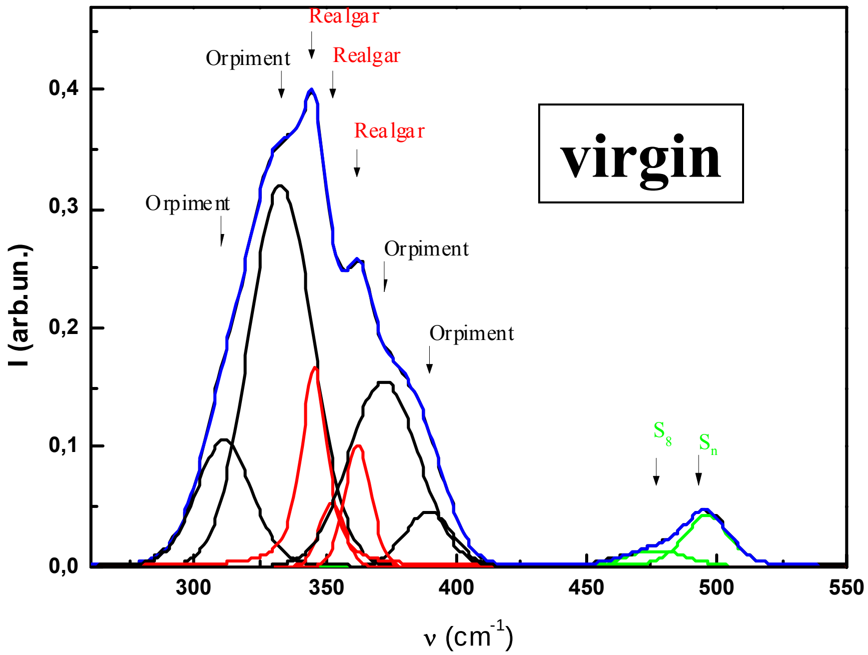
$$(C_2H_5)_2NH + S_n = (C_2H_5)_2NH^+S_n^-$$

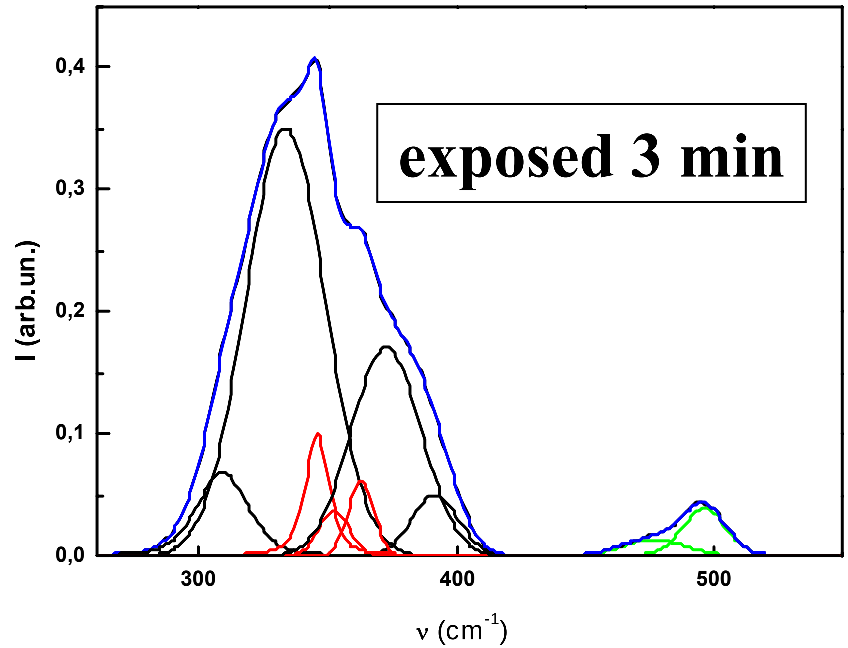
$$(C_2H_5)_2NH^+S_n^- + As_2S_{4/2} = (C_2H_5)_2NH_2^+S^-AsS_{2/2} + (C_2H_5)_2NAsS_{2/2}$$

cage type

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

Raman spectra of $As_{35}S_{65}$ thin film

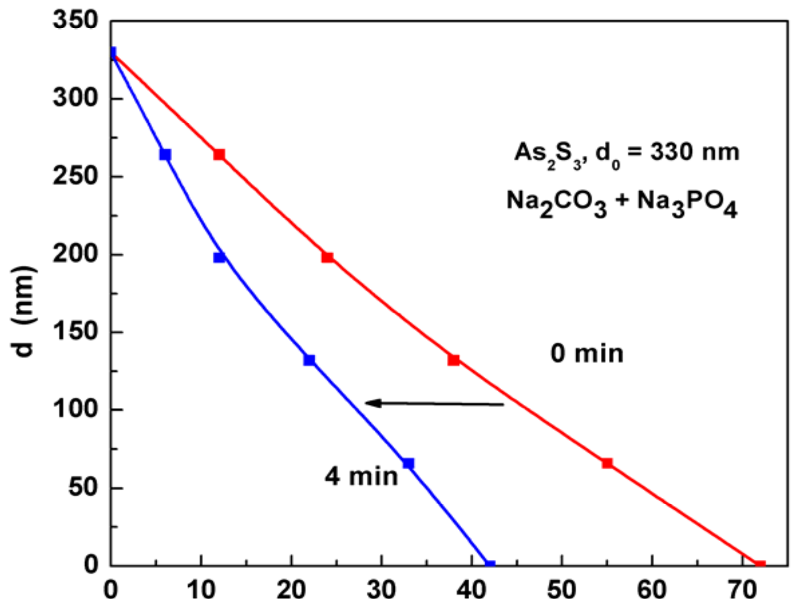




As_2S_3 - orpiment **As_4S_4 cages - realgar**

As-As bonds containing species present even in the structure of S rich As-S films due to nanoscale phase separation of cages

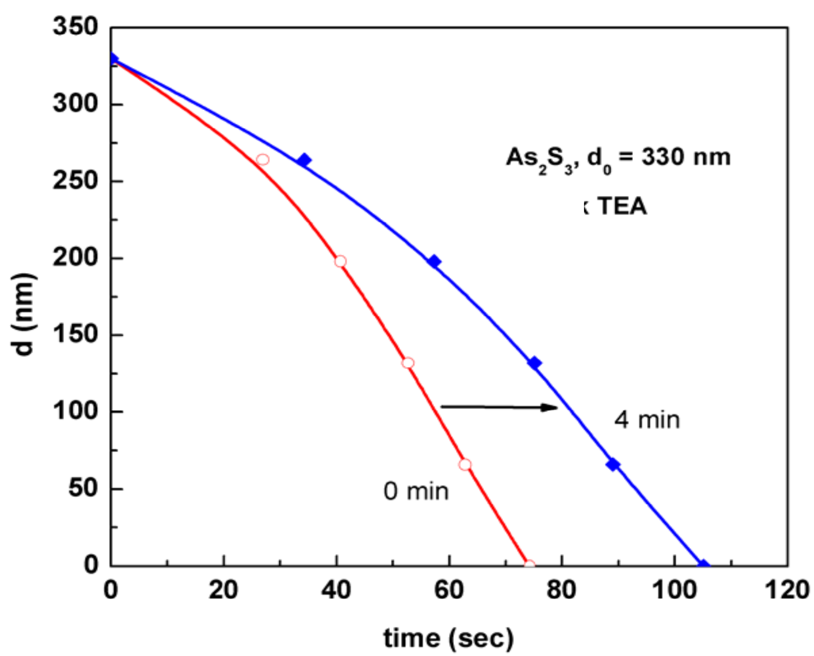
Understanding the selective etching mechanism - first step to achieve extremally high selectivity



Etching bath

Aqueous base

Positive etching



Organic amine base

Negative etching

!!!LOW SELECTIVITY!!!

How to achieve high selectivity of etching?

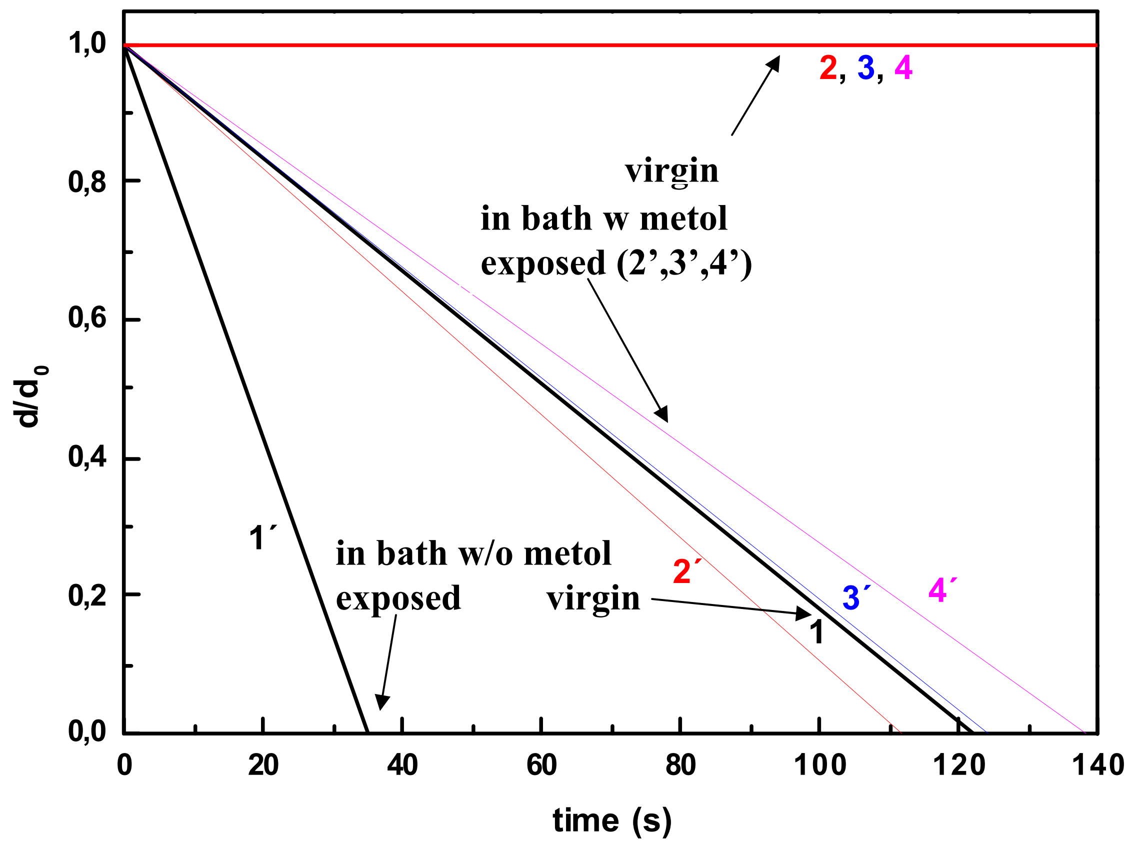
Proper glass composition, proper conditions of deposition, proper exposure …………..

Modification of composition of etching bath

- addition of redox agent into etching bath

- addition of surface active substance (SAS) into etching bath

Selectivity improvement - addition of reducing agent



As_2S_3 film, etched in Na_2CO_3/Na_3PO_4+ metol, pH = 12.
Concentration of metol (g/l): 1,1´- 0; 2,2´ - 0,1; 3,3´ – 0,2; 4,4´ - 0,3;
1´- 4´ exposure with mercury lamp I = 14 mW/cm^{-2}

M. Vlček, M. Frumar, M. Kubový, V. Nevšímalová J. Non-Cryst. Solids, 137-138 (1991) 1035-1036

$$As_2S_3 + 6\ OH^- = AsO_3^{3-} + AsS_3^{3-} + 3\ H_2O$$

$$3\ As_4S_4 + 24\ OH^- = 4\ AsO_3^{3-} + 4\ AsS_3^{3-} + 4\ As + 12\ H_2O$$

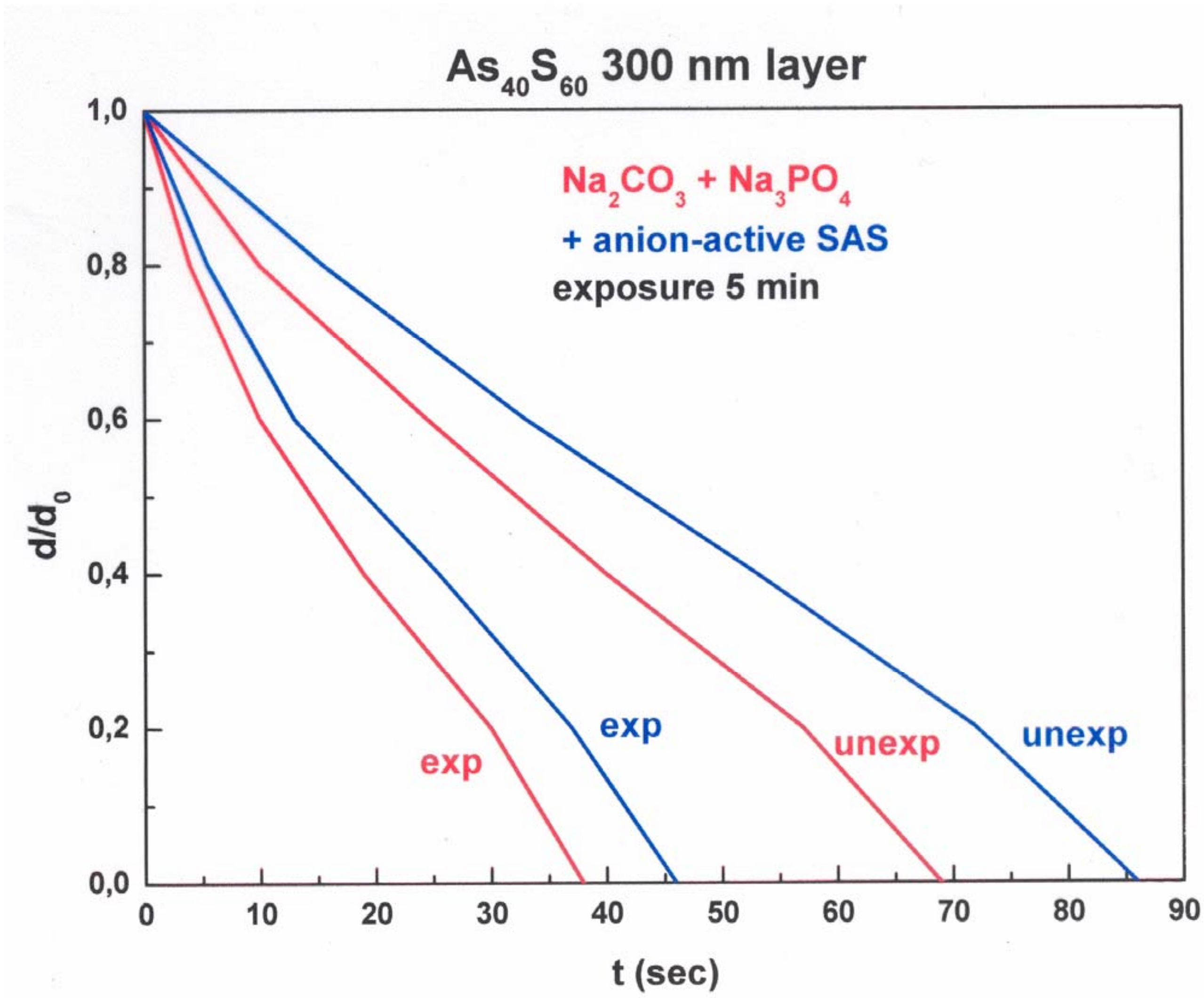
Selectivity improvement - addition of surface active substancies (SAS)

Anion-active SAS – **sodium p-dodecylbenzenesulphite**
disodium bis-2-ethylhexylsuccinic disulphite

Non-ionic SAS - **oxyethyl derivates of monoethanolaminesters**

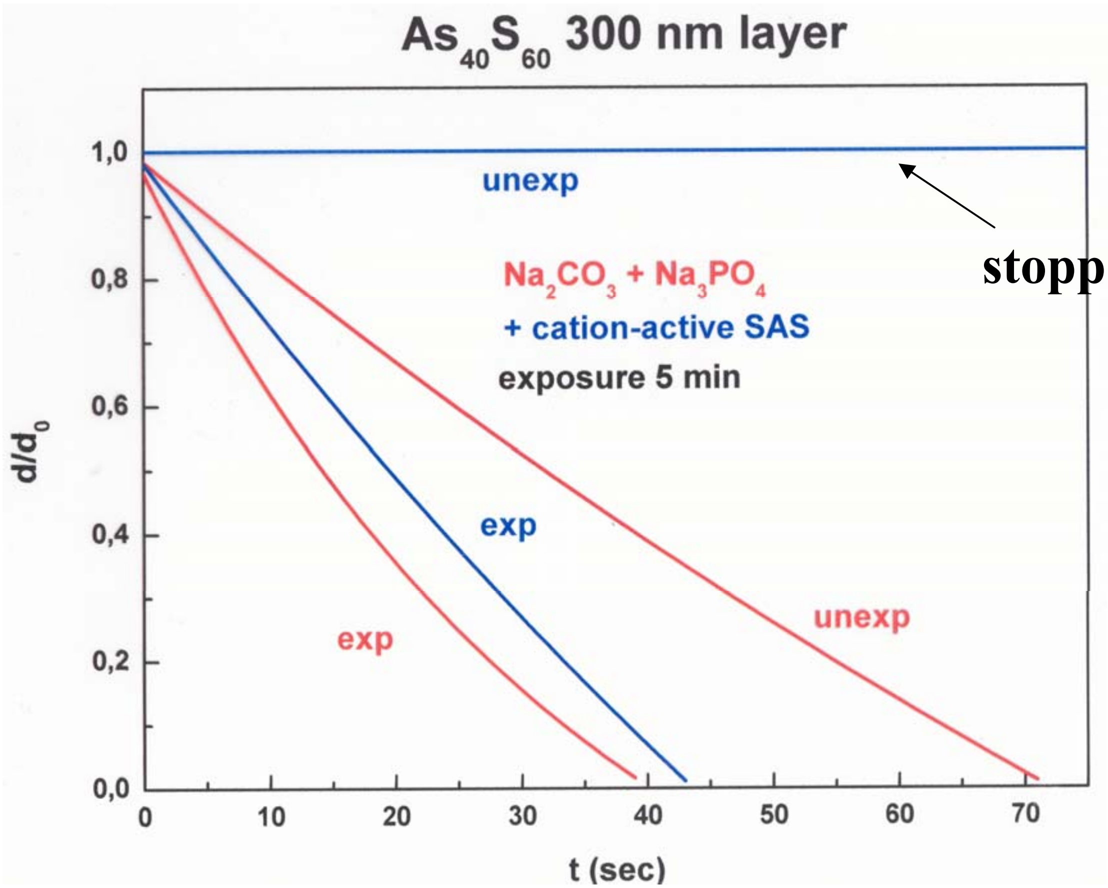
Cation-active SAS - **cetyltrimethylammonium bromide**
benzenedodecyldimethylammonium bromide
carboxypentadecyl-trimethylamonium chloride

Addition of anion-active and/or non-ionic SAS



no selectivity of etching improvement – only slower rate for both

Addition of cation-active SAS



stopped fully!

cetyltrimethylammonium bromide

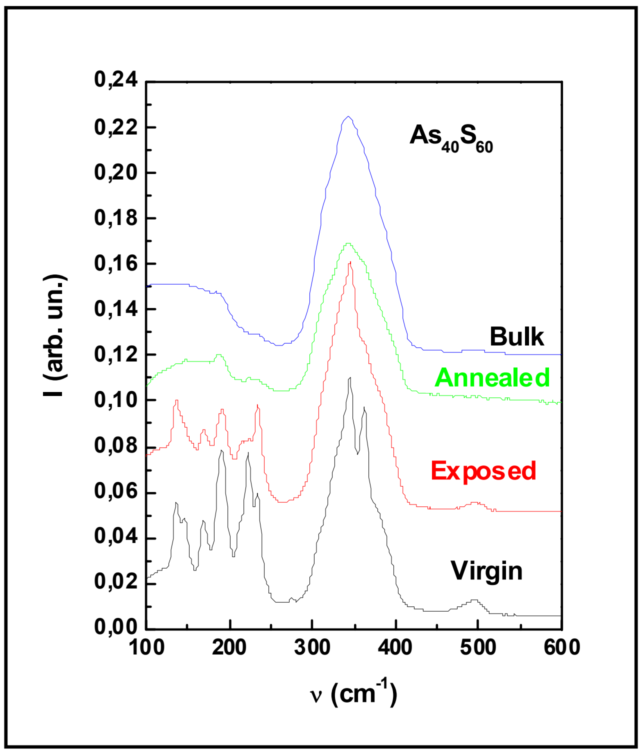
M. Vlček, P. J. S. Ewen, T. Wagner J. of Non-Cryst. Solids 227-230 (1998) 743-747

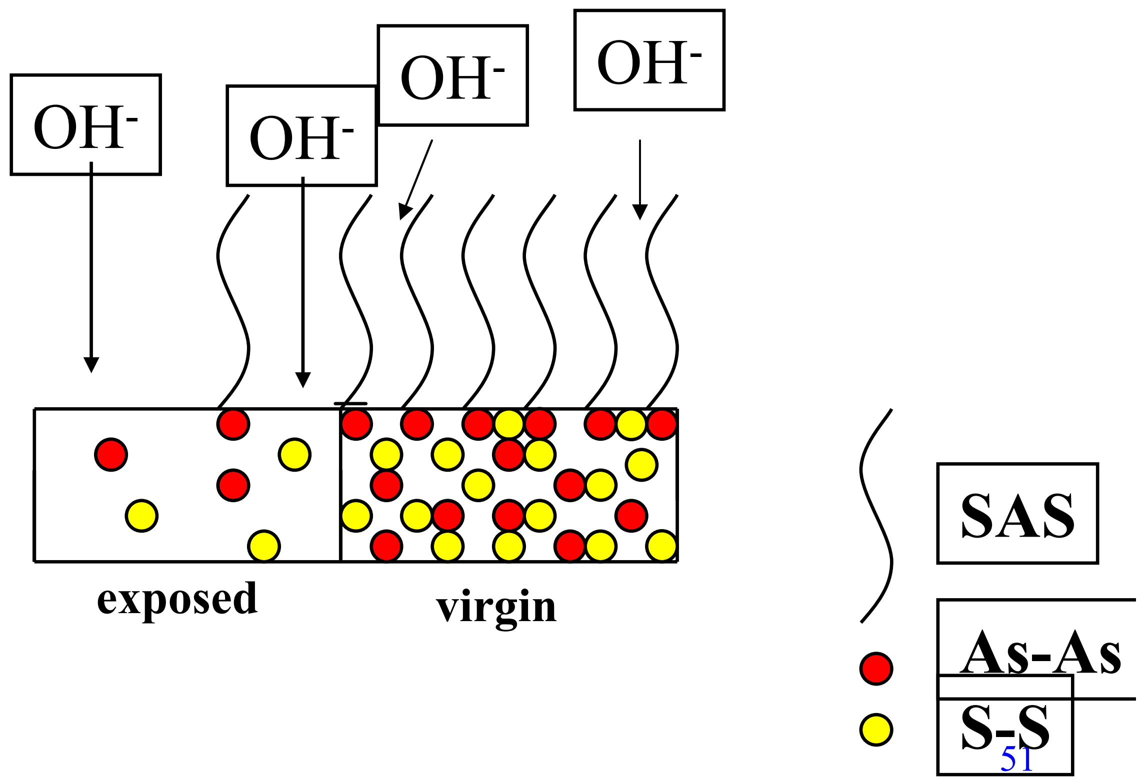
It works!!! But how???

How it works? What is function of cation-active SAS ?

Structure of SAS: quaternary ammonium salts with long hydrophobic chain

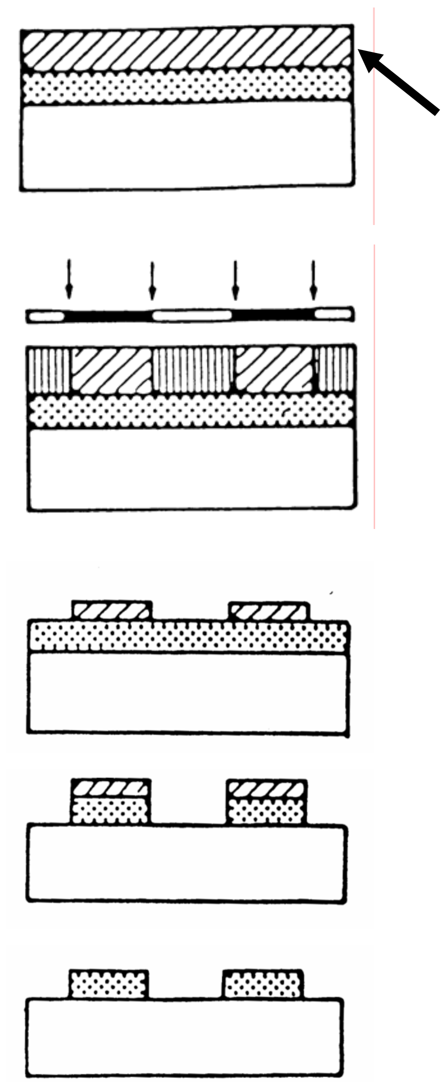
Preferably sorbed at the surface of unexposed samples, hydrophobic chain repulse OH^- ions, etching rate decreases significantly





Conclusion - positive wet lithography

exploit photostructural change in ChG and application of SAS produce extremally high positive selective etching in aqueous alkaline solvents



deposition of ChG

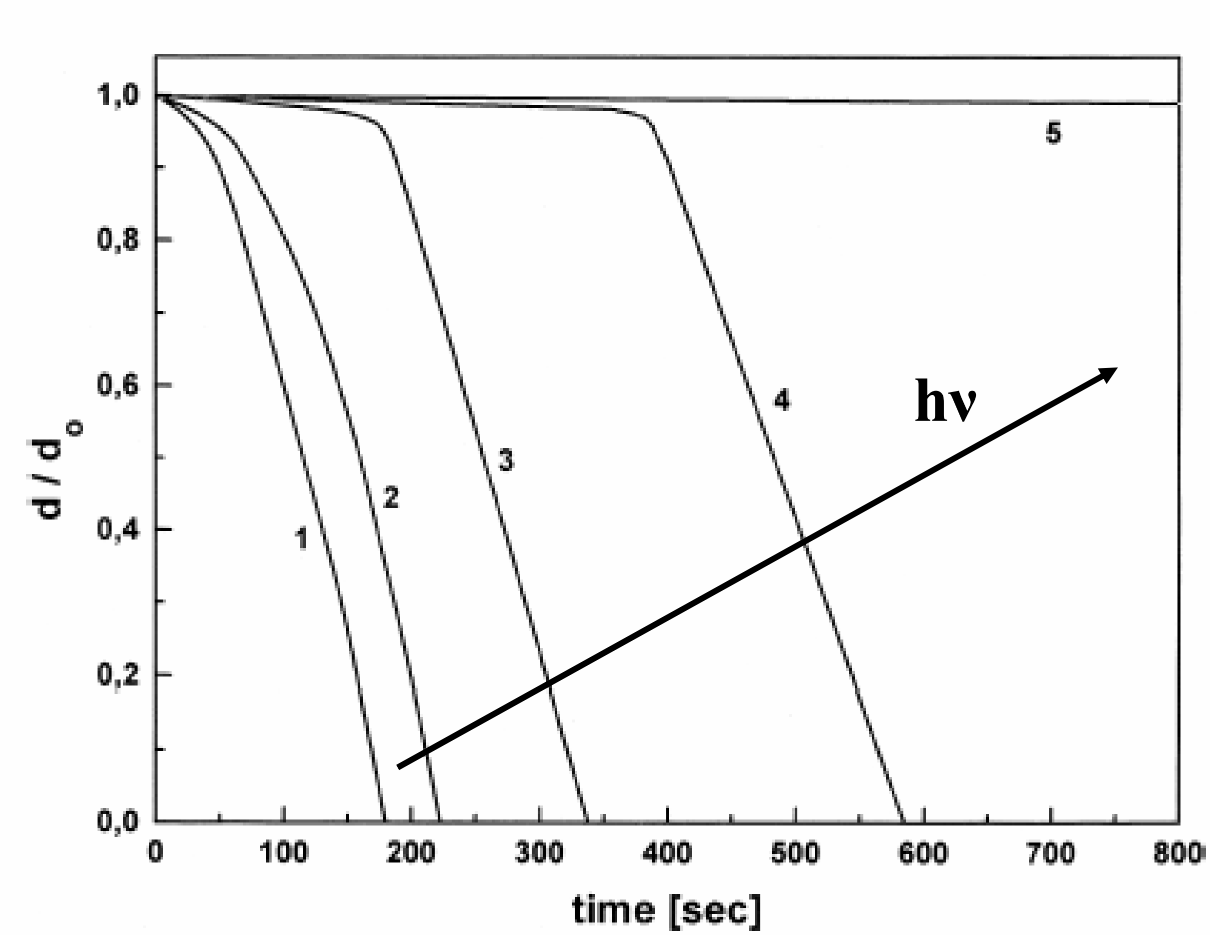
exposure

etching by aqueous alkaline solution

substrate (Cr, SiO_2, Si_3N_4…) etching

ChG layer removal

Selectivity improvement – proper composition of CHG and proper exposure source



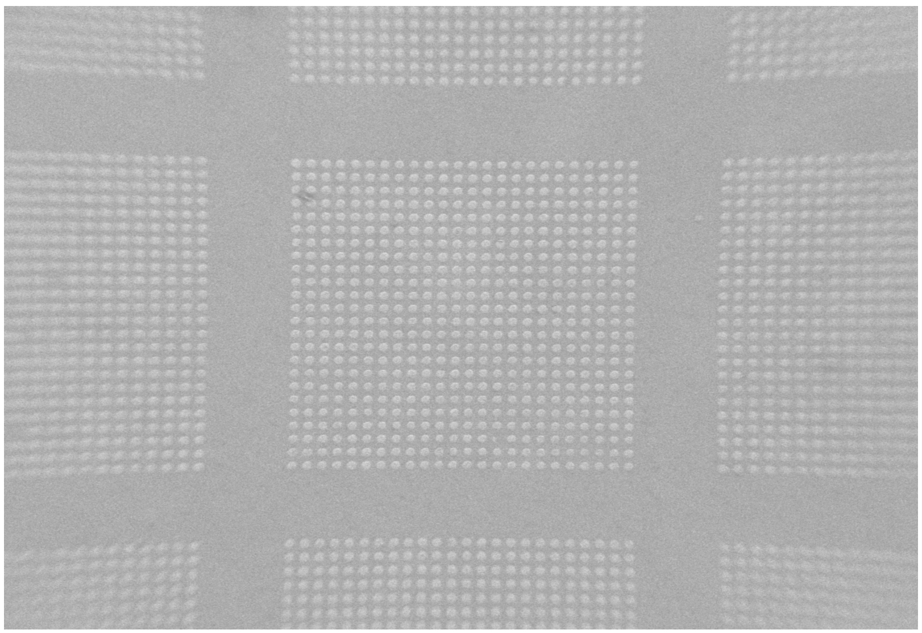
$As_{33}S_{67}$
$d_o = 3.7\ \mu m$

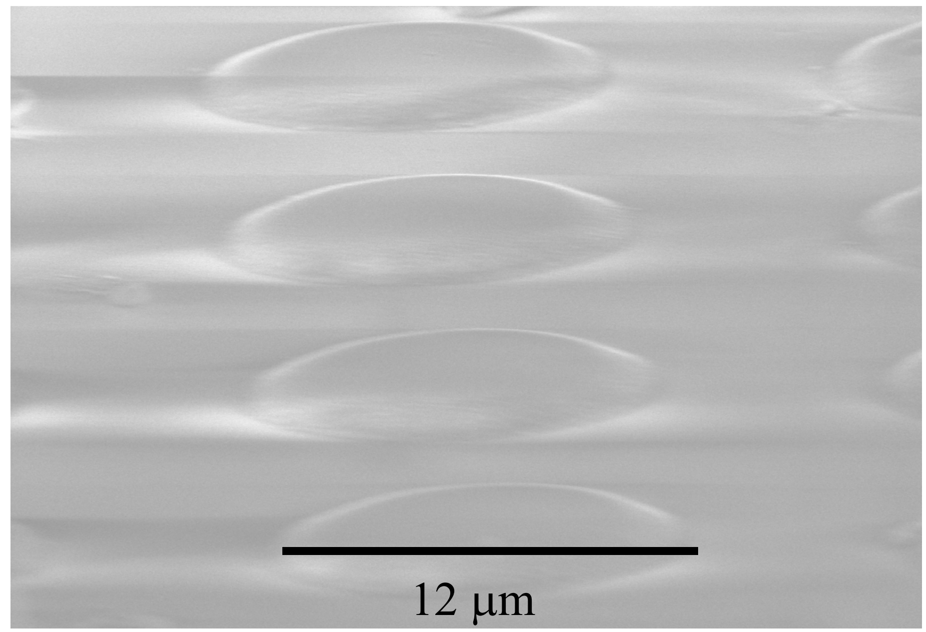
UV lamp
Exposure in air (sec)
1 – 0
2 – 30
3 – 60
4 – 90
5 – 120
TEA based solvent

postponing in etching proportional to exposure dose
even shaped structures can be etched

M. Vlček, P. J. S. Ewen, T. Wagner J. of Non-Cryst. Solids 227-230 (1998) 743-747

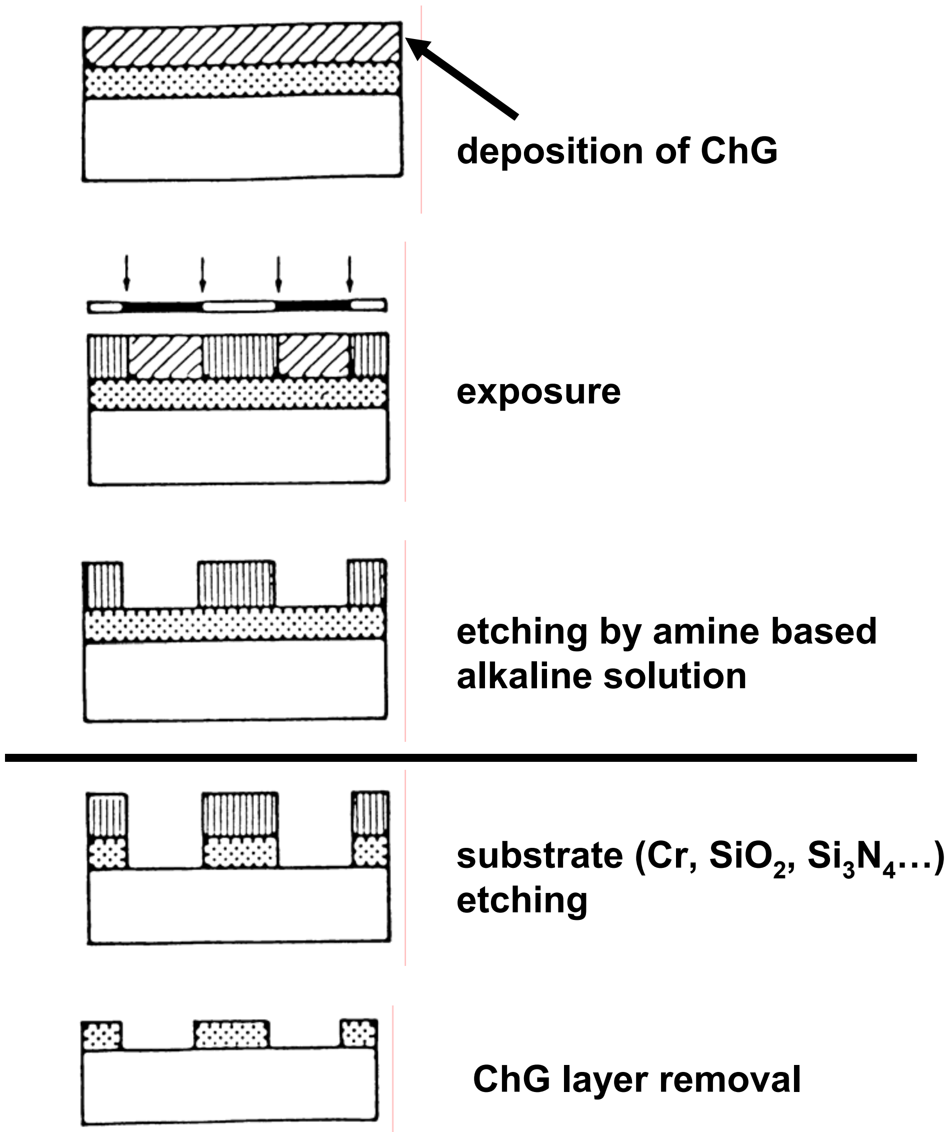
Micro-lens Array
made by exposure with Halogen Lamp through Grey Mask



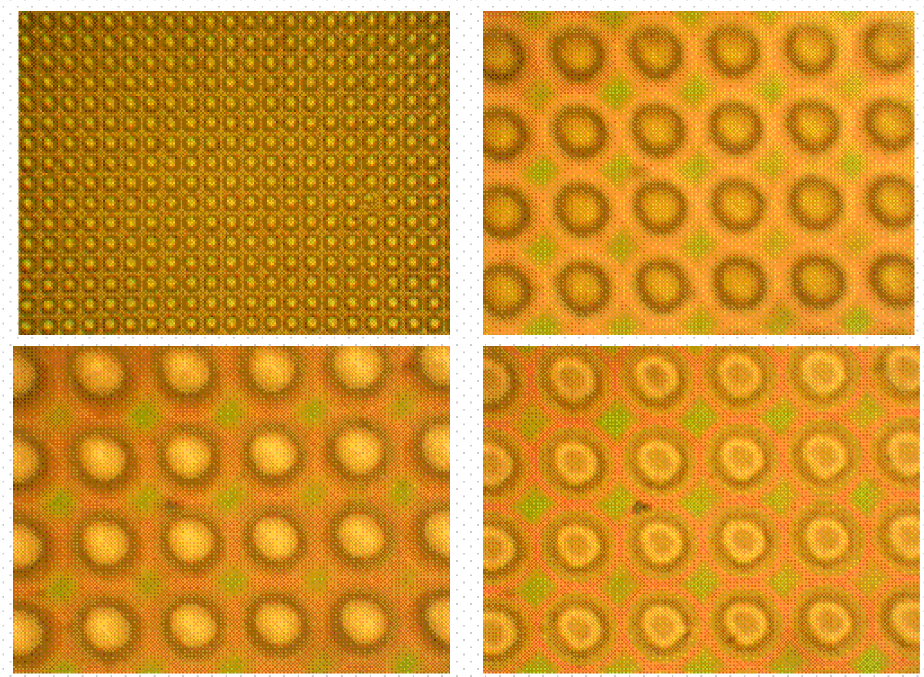


Conclusion - negative wet lithography

exploit photostructural change in ChG extremally high negative selective etching in non-aqueous alkaline solvents can be achieved



Microlithography with gray scale mask



microlens arrays (12 μm diameter) in a thin $As_{35}S_{65}$ film, fabricated using a gray Cr mask. The focusing action of light by the lenses is clearly seen.

Wet **micro**lithography example – direct laser writing

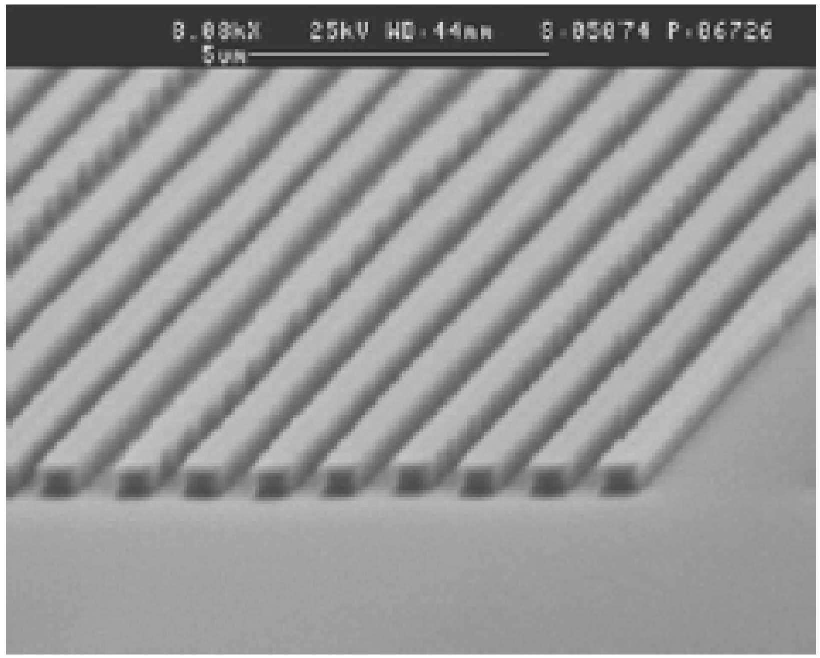
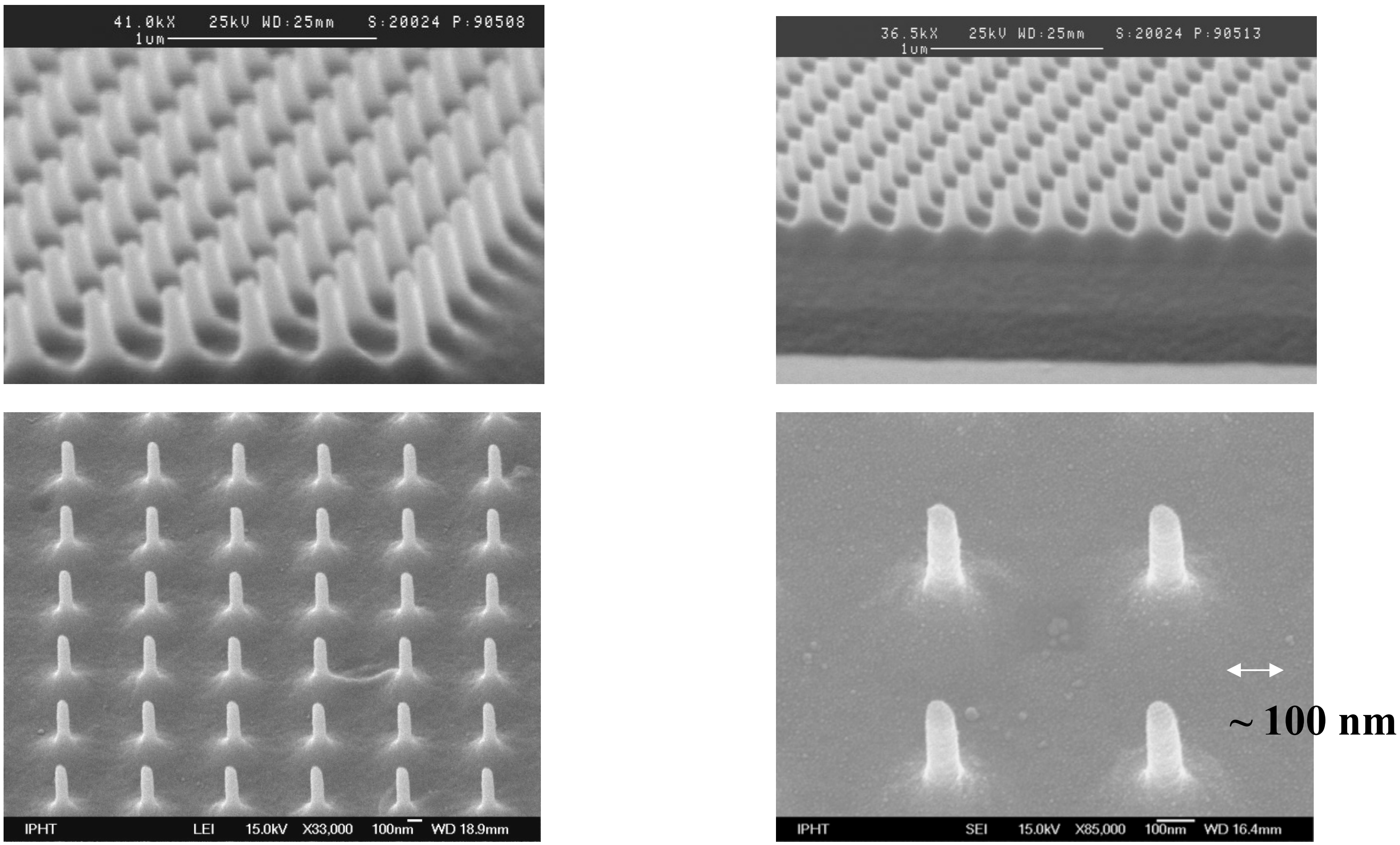


Fig.1. SEM picture of a gold coated binary grating with a period of 1.26 µm and a ridge width of 750 nm etched 550nm deep into $As_{35}S_{65}$

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

Electron beam wet **nano**lithography



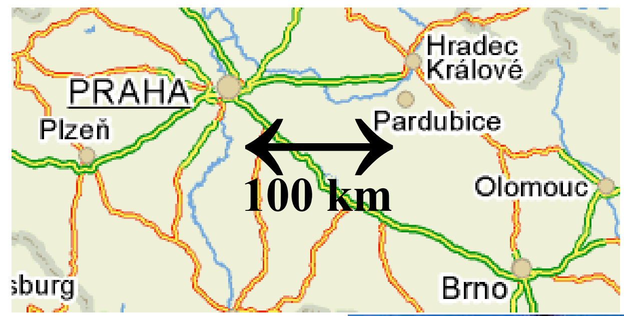
SEM pictures of pillar arrays in quadratic arrangement etched into $As_{35}S_{65}$. (a): diameter 122 nm, depth 410 nm, and period 400 nm (b): diameter 100 nm, depth 410 nm, and period 300 nm (c,d): diameter less than 100 nm, depth 300 nm, and period 350 nm, displayed at different magnifications

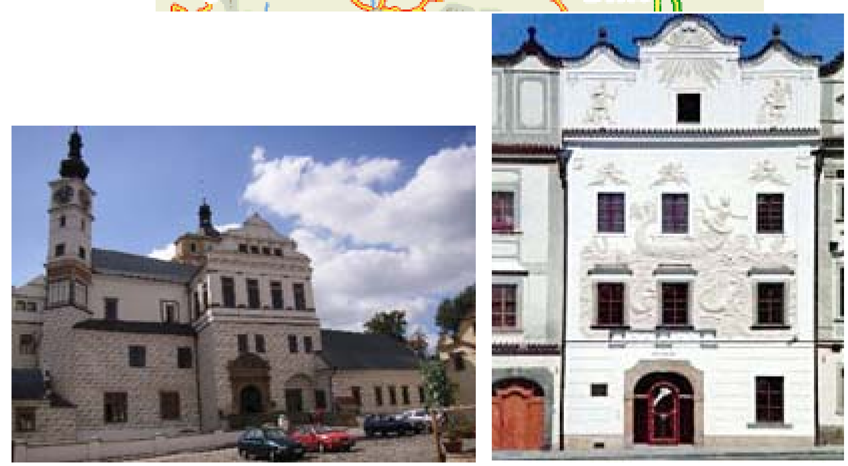
S. Schröter, M. Vlcek, R. Pöhlmann, T. Glaser and H. Bartelt: Proceedings of MOC´04, Jena, Germany, September 2004

!!!Wet macrolithography!!!

Green tower, Pardubice, Czech Republic

in real **in chromium**

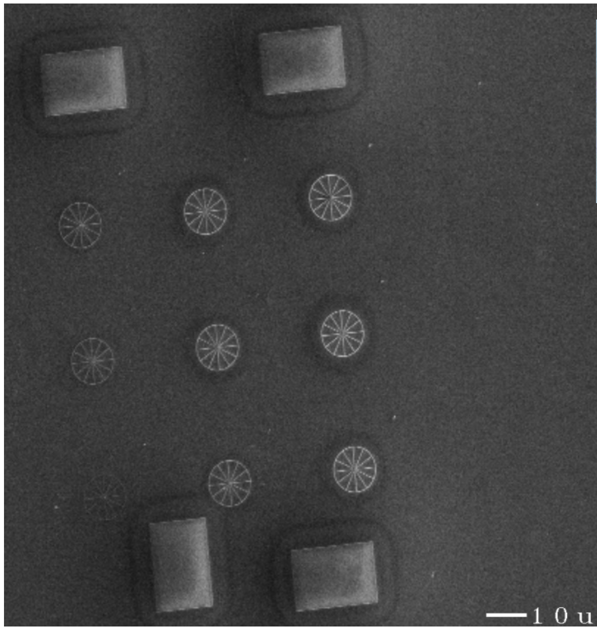


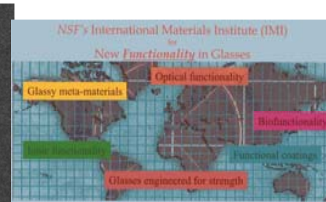


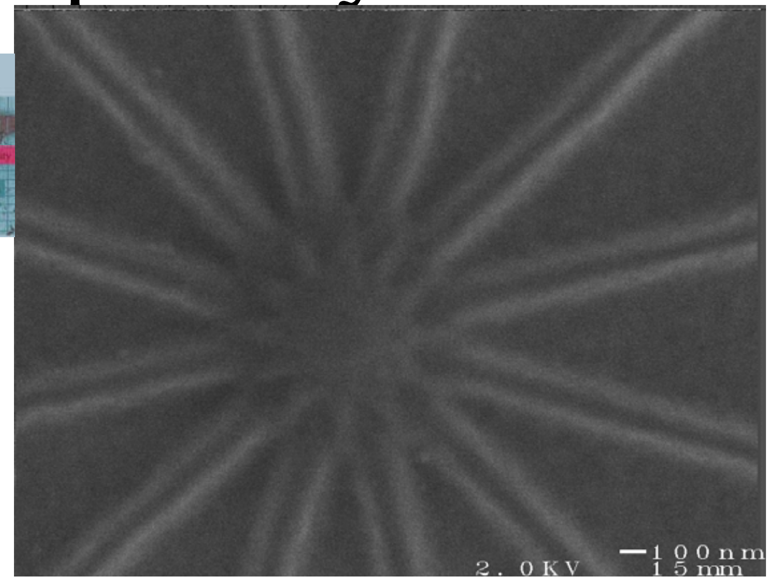
http://www.pardubice.cz/

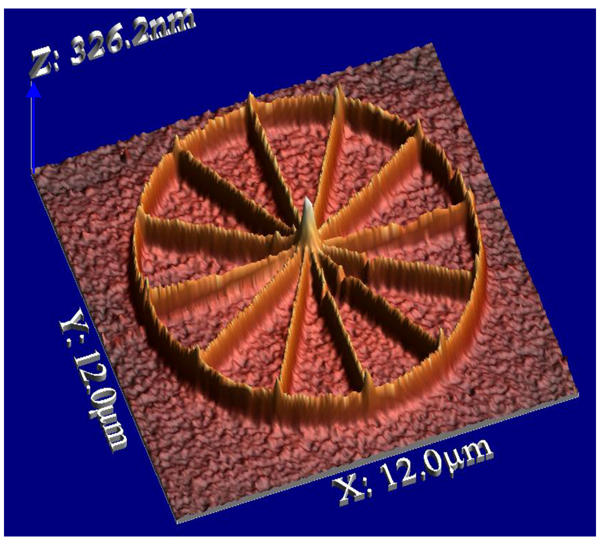
What is the resolution limit of CHG etching?

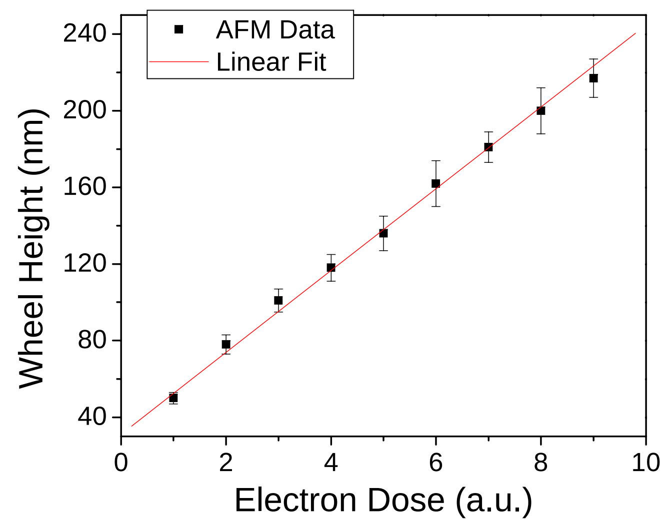
Resolution capability







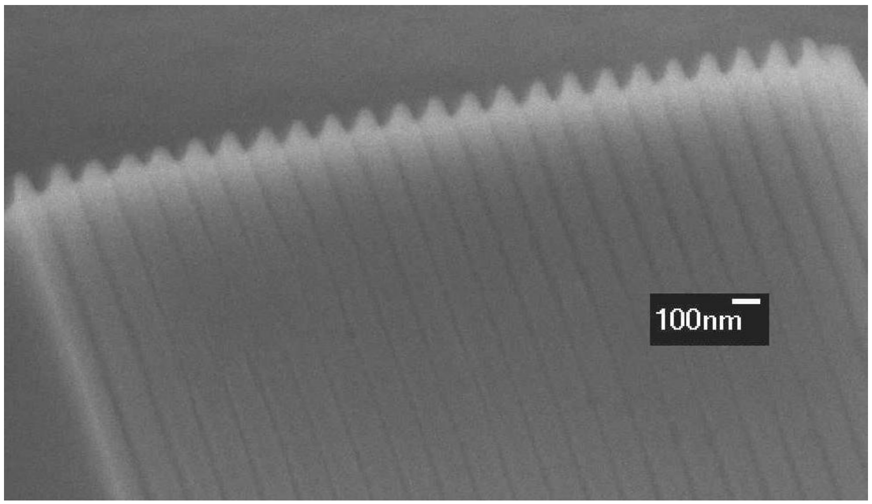




M. Vlcek, H.Jain J. of Optoelectronics and Advanced Materials 8 (6) (2006) 2108 - 2111

Resolution limit – 7 nm???

or less????



SEM picture of a nanograting fabricated in As-S film by electron beam exposure followed by development in amine based solvent. Stage tilt of 45º at 15 kV. Grooves width 14 nm.

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

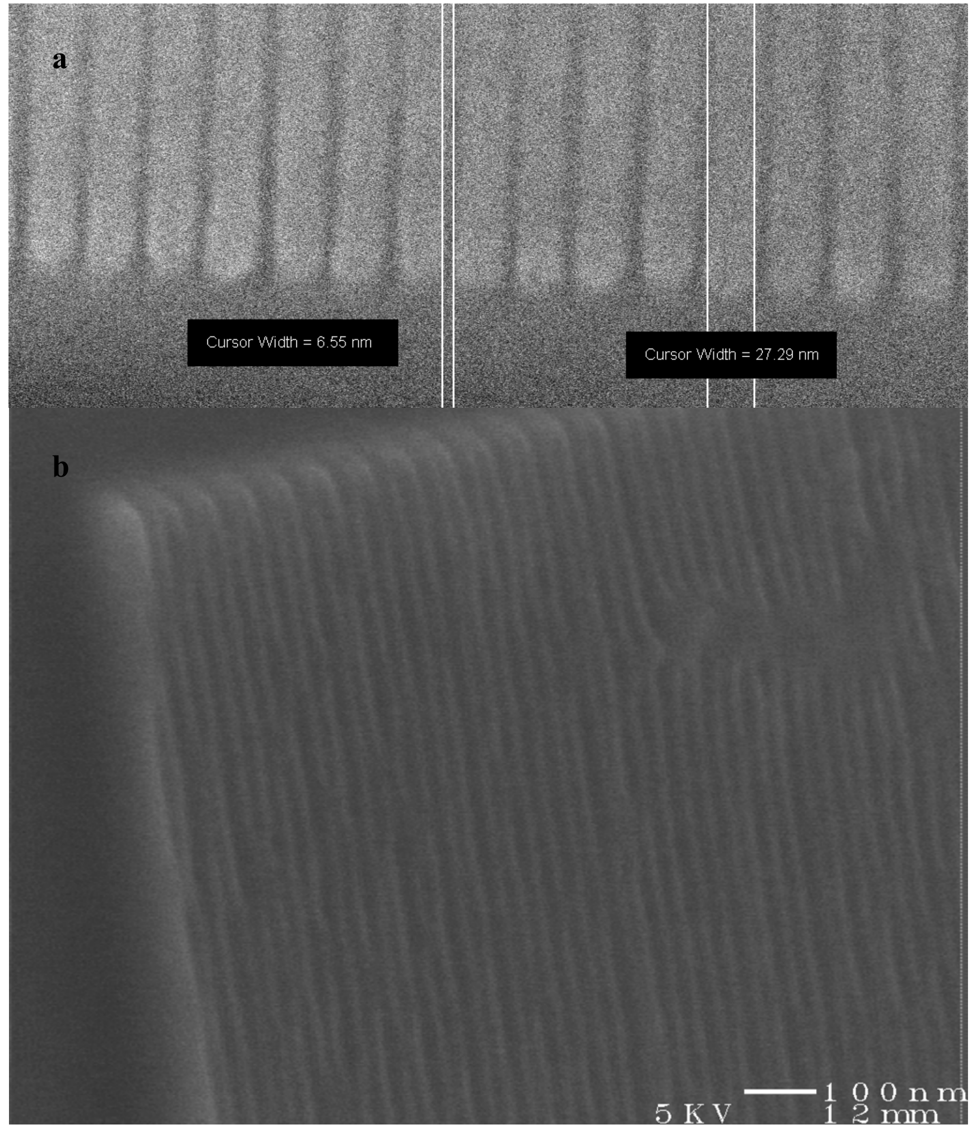
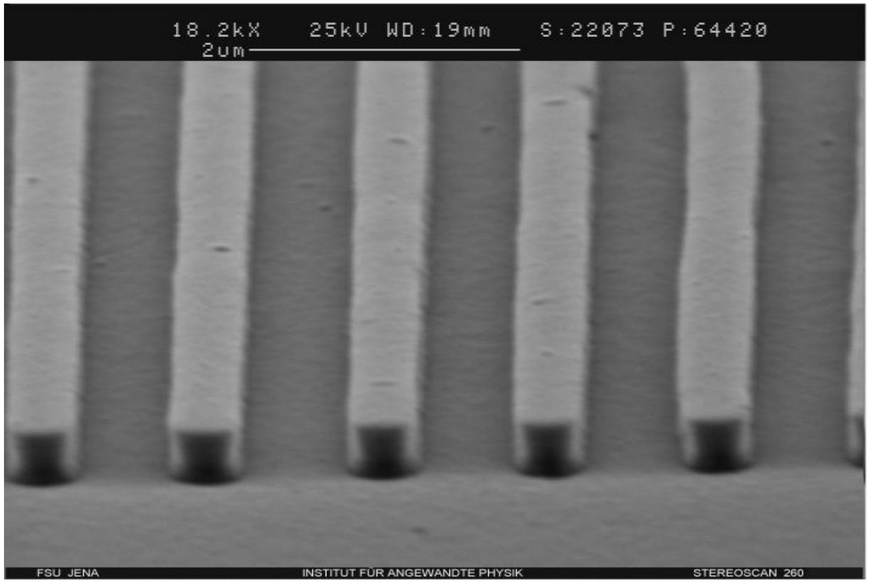


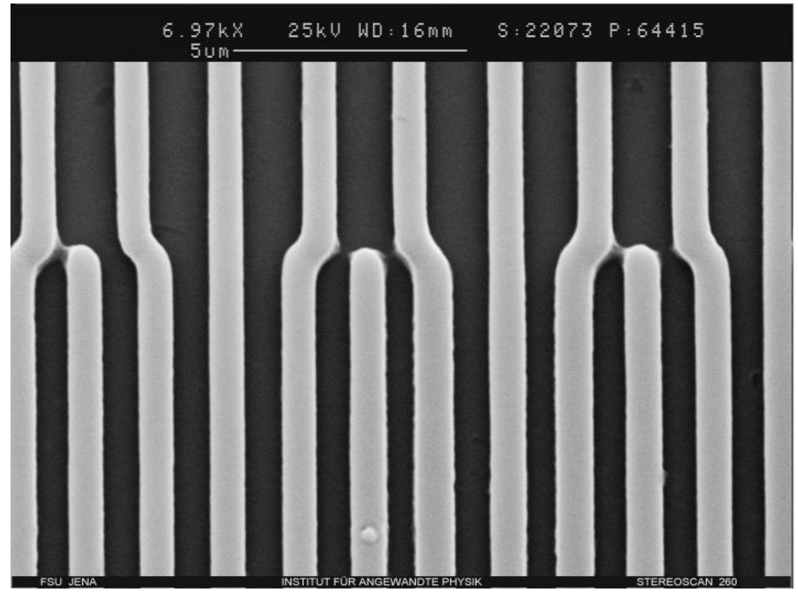
Figure 2(a) shows various vertical lines that are 27 nm wide and have gap separations of only 7 nm. In Figure 2(b) a tilted SEM image shows the topography of the grating structure. Heights of the individual lines ~80-90 nm tall

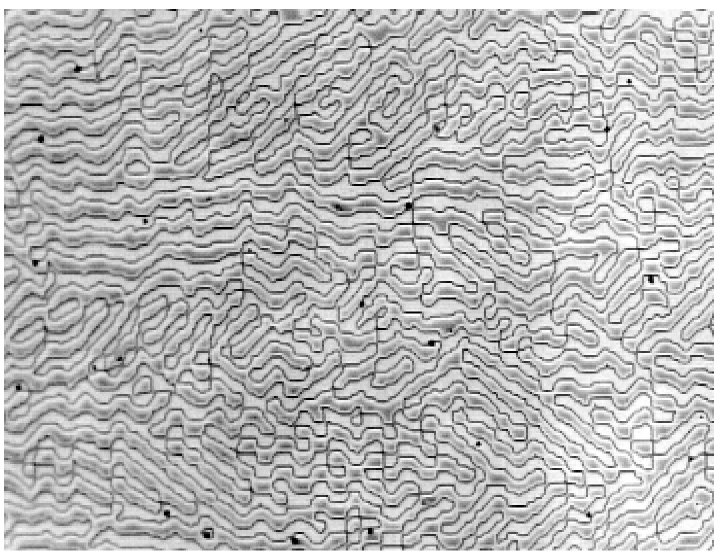
J.R. Neilson, A. Kovalskiy, M. Vlček, H. Jain, F. Miller J. of Non-Cryst. Solids 353 (13-15) (2007) 1427-1430

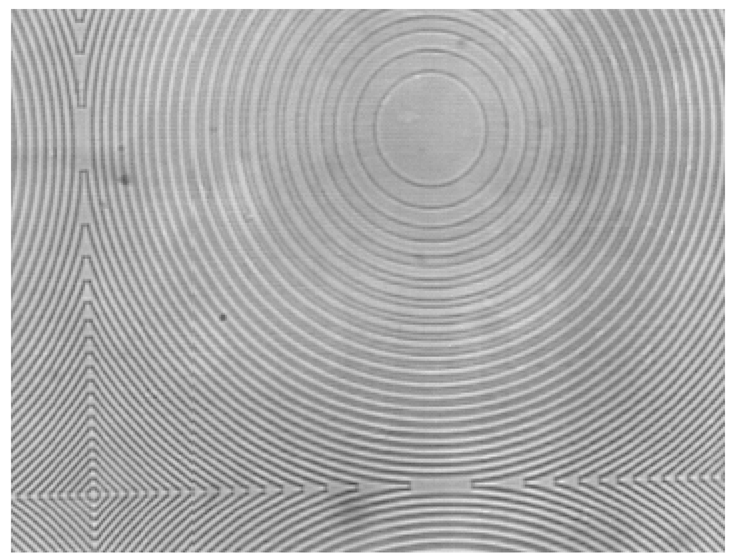
Some examples of micro and nanostructuring of CHG and/or their exploitation to transfer patterns into other materials

Direct laser writing at 442 nm, wet etching



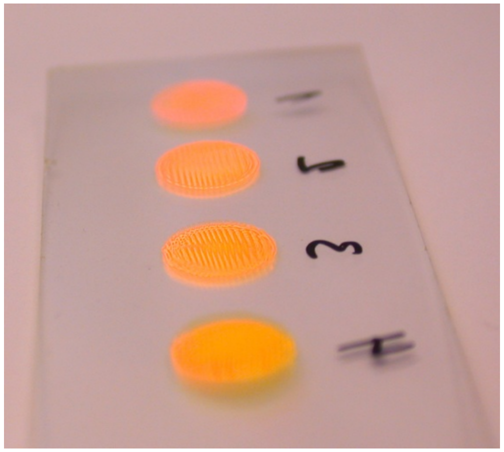


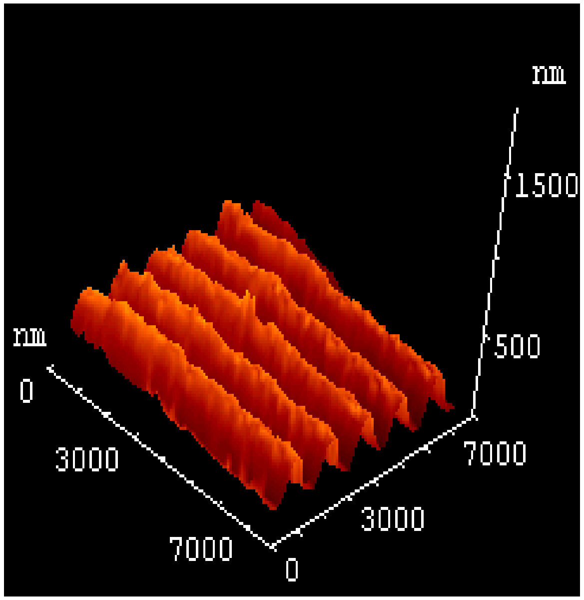


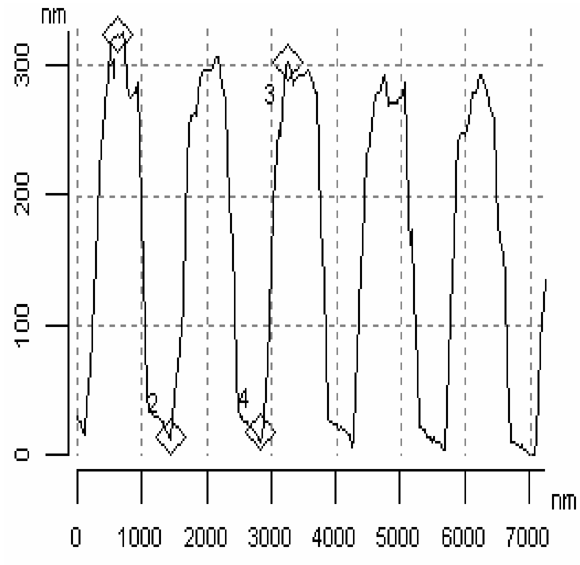


c

Holographic exposure







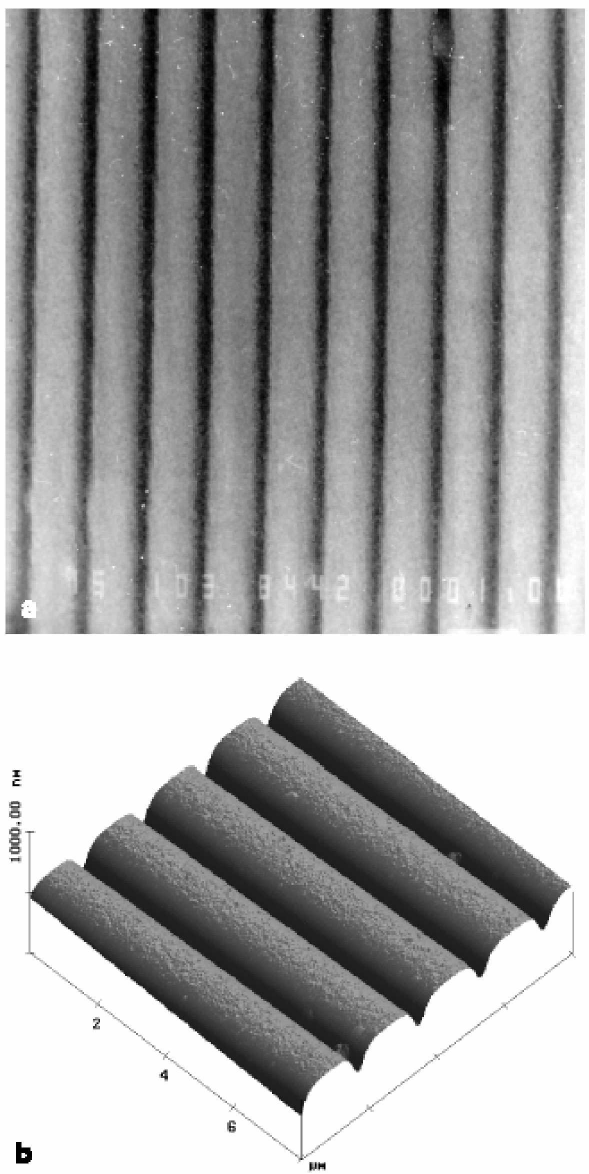


Fig. 2. SEM image (a) and AFM image (b) of the holographic grating with spatial frequency 1200 mm^{-1} (a) and 600 mm^{-1} (b).

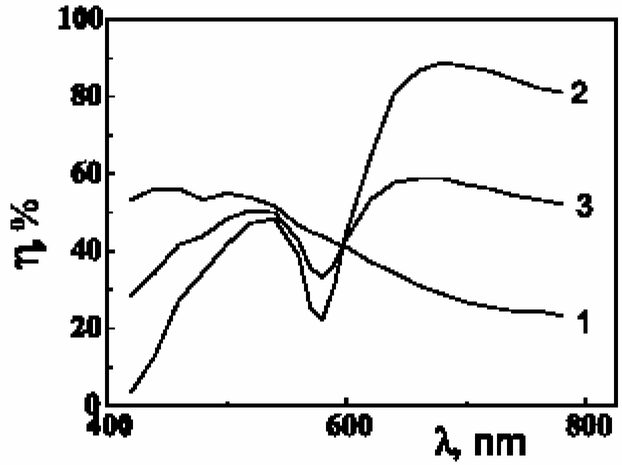


Fig. 3. Spectral distribution of the diffraction efficiency η for the grating with spatial frequency 1350 mm^{-1}. (1) P-polarization; (2) S-polarization; (3) non-polarized light.

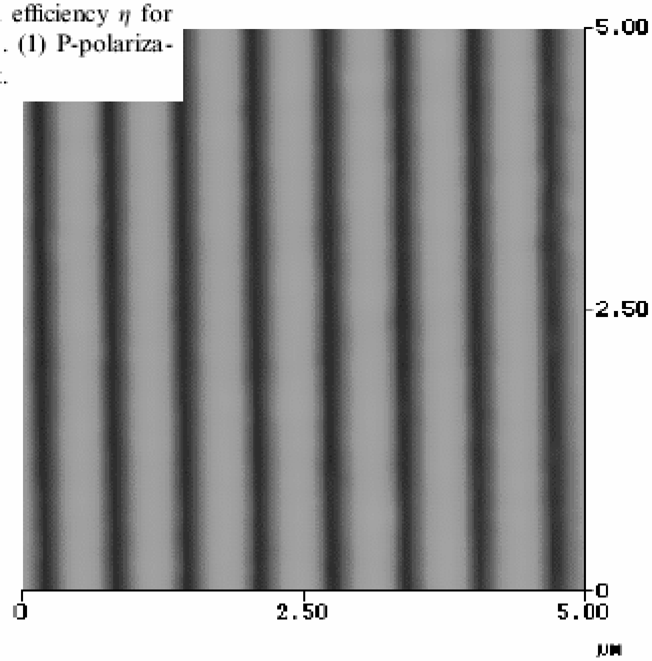


Fig. 4. AFM image of polymer copy of master grating with spatial frequency 1600 mm^{-1}.

A.V. Stronski, M. Vlcek, A. Sklenar, P.E. Shepeljavi, S.A. Kostyukevich, T. Wagner
J. of Non-Cryst. Solids 266-269 (2000) 973-978

DLW of 3D photonic crystal structures

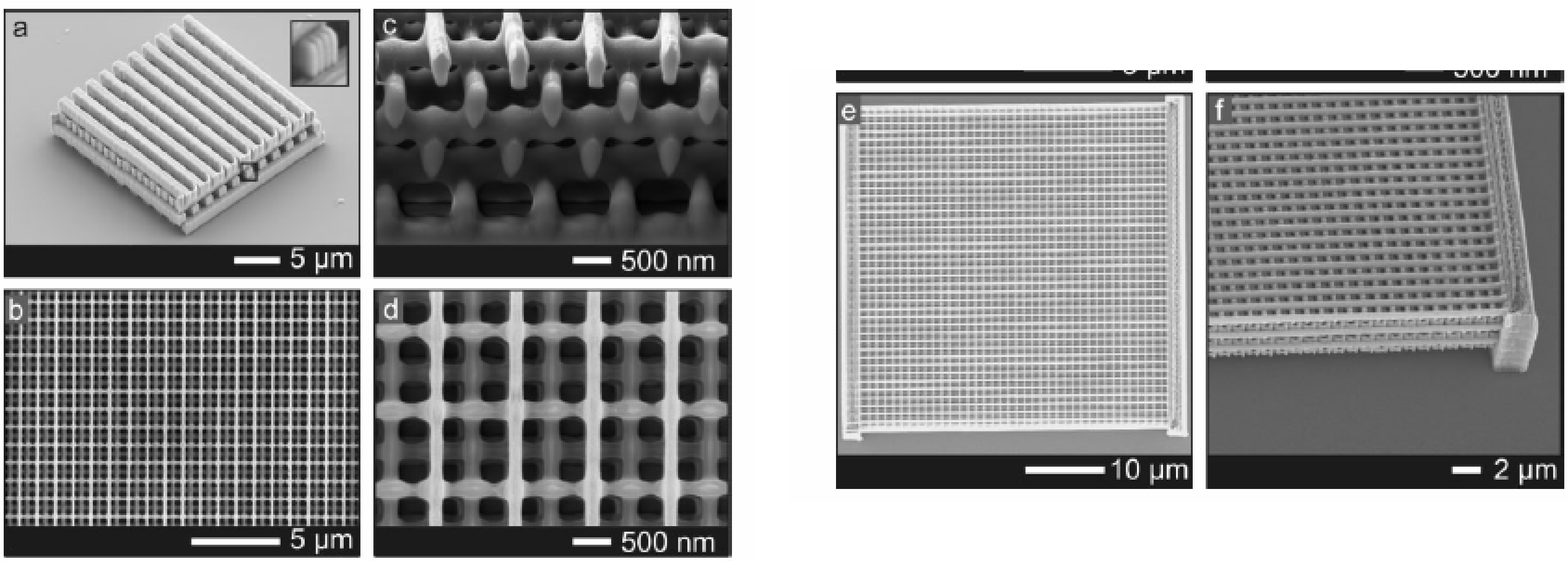


Figure 3. Scanning electron microscopy images of As_2S_3 woodpiles. a) Woodpile with rod distance $a = 2$ µm to illustrate the construction principle of the rods. Each rod is made from eight parallel subrods to yield a rod aspect ratio of almost 1.0 (see inset). b) Top view of a woodpile with rod distance $a = 1$ µm. Note the perfectly straight rods. c) Focused-ion-beam cross section of the woodpile in (b). d) Close up of (b). Note the smoothness of the rod surfaces. e) Top view of a woodpile similar to the one shown in (b) but with a 40 µm × 40 µm footprint and twelve layers. f) Side view of the woodpile shown in (e). The walls merely serve as a support for the woodpile, which is intentionally raised off the substrate.

S. Wong at al. Adv. Matter. 18 (2006) 265 - 269

Transparent and semitransparent holograms

US006452698B1

(12) **United States Patent**
Vlcek et al.

(10) **Patent No.: US 6,452,698 B1**
(45) **Date of Patent: Sep. 17, 2002**

(54) **TRANSPARENT AND SEMITRANSPARENT DIFFRACTIVE ELEMENTS, PARTICULARLY HOLOGRAMS AND THEIR MAKING PROCESS**

(75) Inventors: **Miroslav Vlcek**, Pardubice (CZ); **Ales Sklenar**, Hradec Králové (CZ)

(73) Assignee: **OVD Kinegram AG**, Zug (CH)

4,856,857	A		8/1989	Takeuchi et al.	359/3
5,138,604	A	*	8/1992	Umeda et al.	283/86
5,465,238	A	*	11/1995	Russell	359/20
5,496,072	A		3/1996	Yamauchi et al.	283/86
5,745,475	A	*	4/1998	Ohno et al.	369/275.4
6,036,807	A	*	3/2000	Brongers	359/2

FOREIGN PATENT DOCUMENTS

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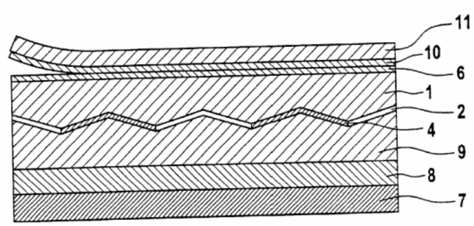
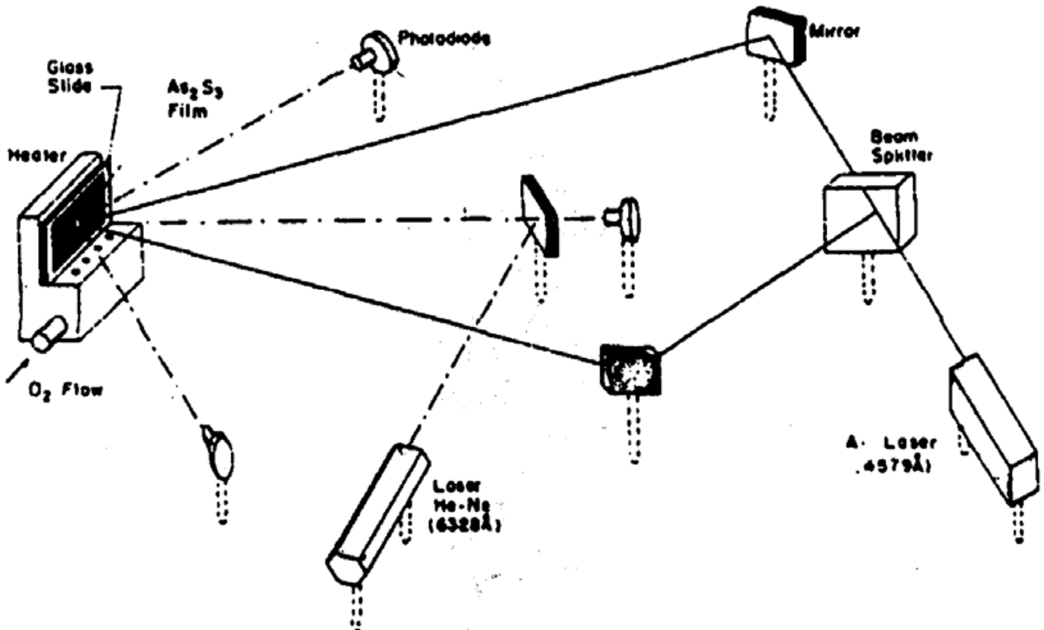


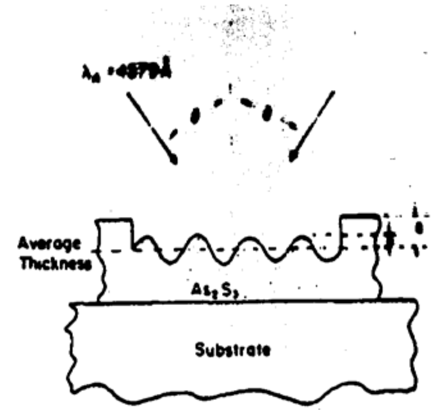
M. Vlček, A. Sklenář: Transparent and Semitransparent Diffractive Elements, Particularly Holograms and Their Making Process, US patent 6,452,698 B1, 17. 9. 2002. *Canada (CA 2,323,474), Japan (JP 2002 507770 T), EU (EP1062547o), former USSR states (EA2393), Slovakia (SK 13552000)*

Direct microstructuring

(no etching best etching)

Photoinduced local oxidation

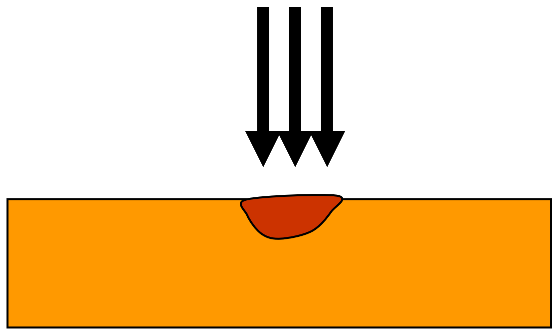




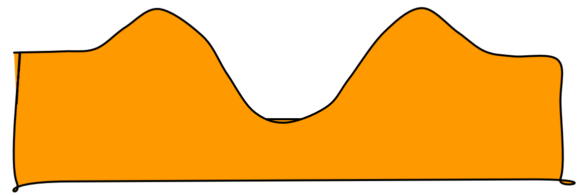
$$2\,As_2S_3 + 3\,O_2 \xrightarrow{h\nu} As_4O_6\uparrow + 3\,S_2\uparrow$$

M. Janai et al.: Optics Letters 2 (2) (1978) 51

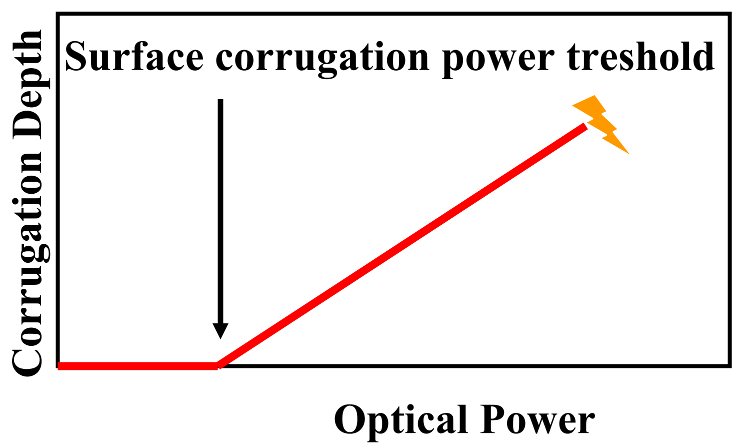
Photoinduced local corrugation by high energy high intensity beam



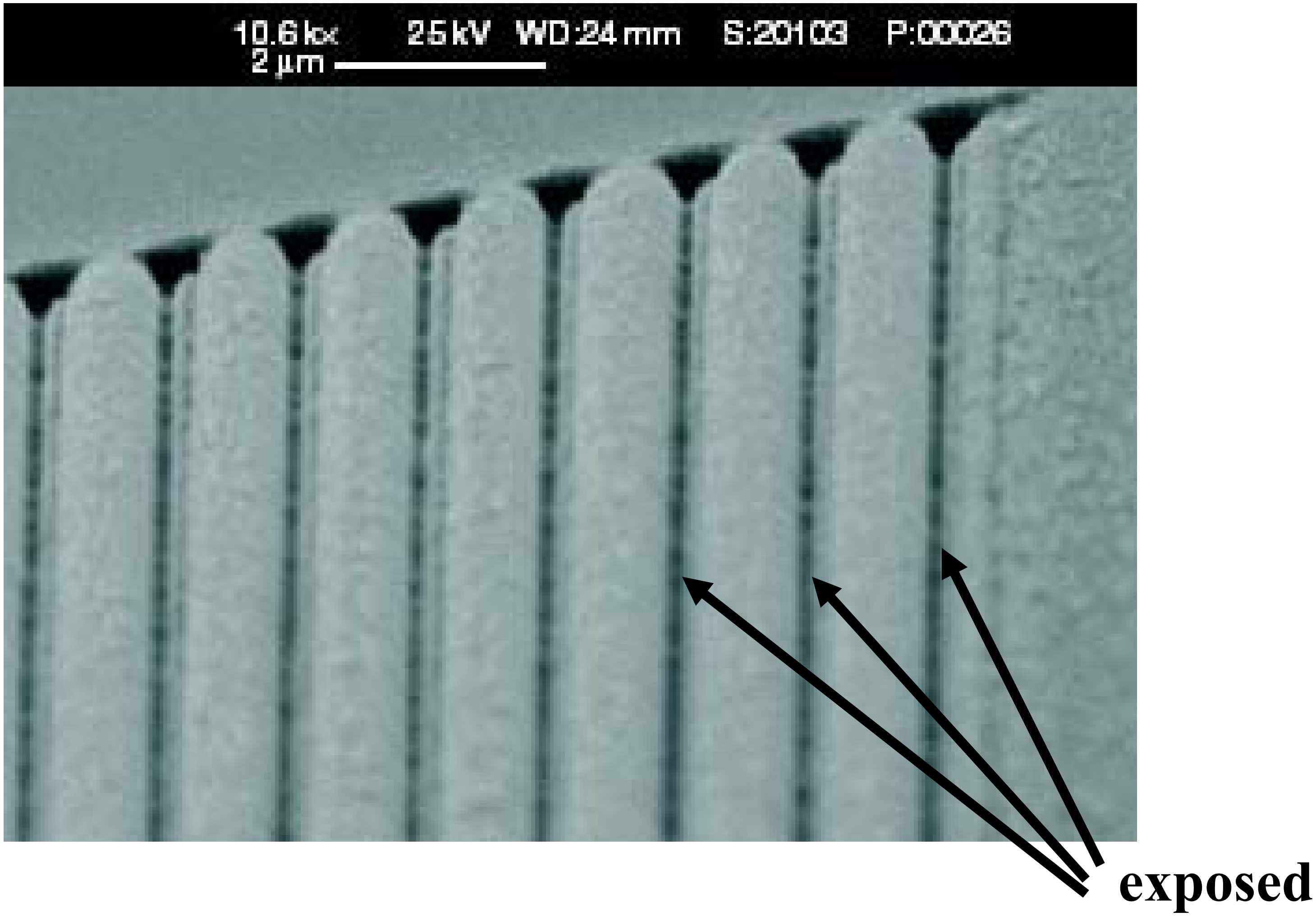
Local heating close to T_g



Corrugated result



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



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. Schroter, S. Fehling, R. Pohlmann and M. Vlcek ELECTRONICS LETTERS 40 (3) (2004) 176 - 177

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

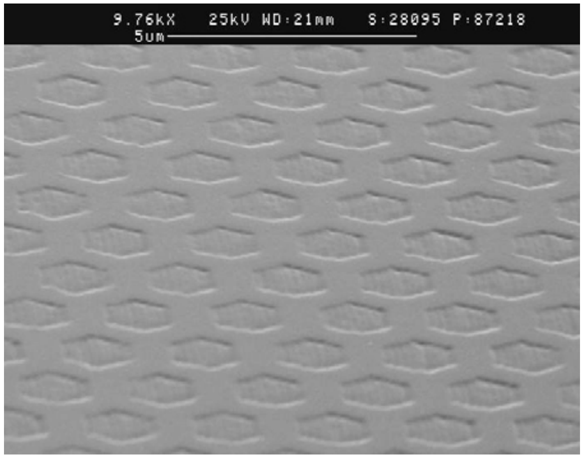
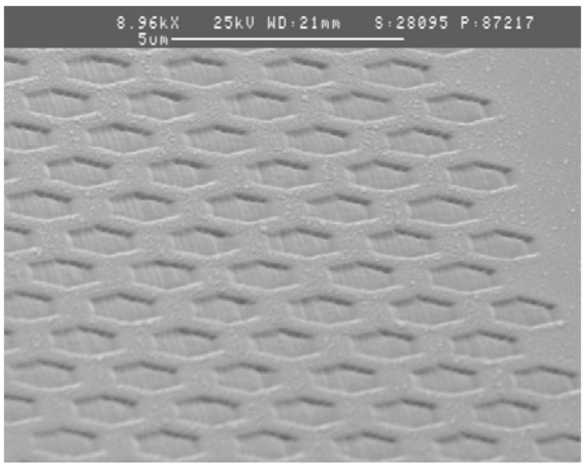
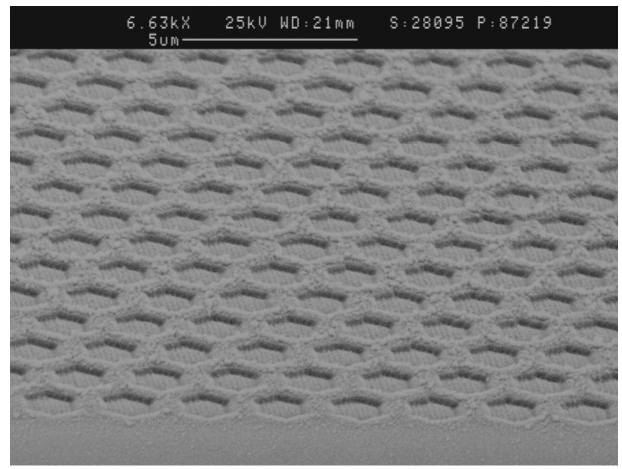


Table 1
Surface corrugation threshold powers

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/cm² and 2.6 J/cm².

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

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

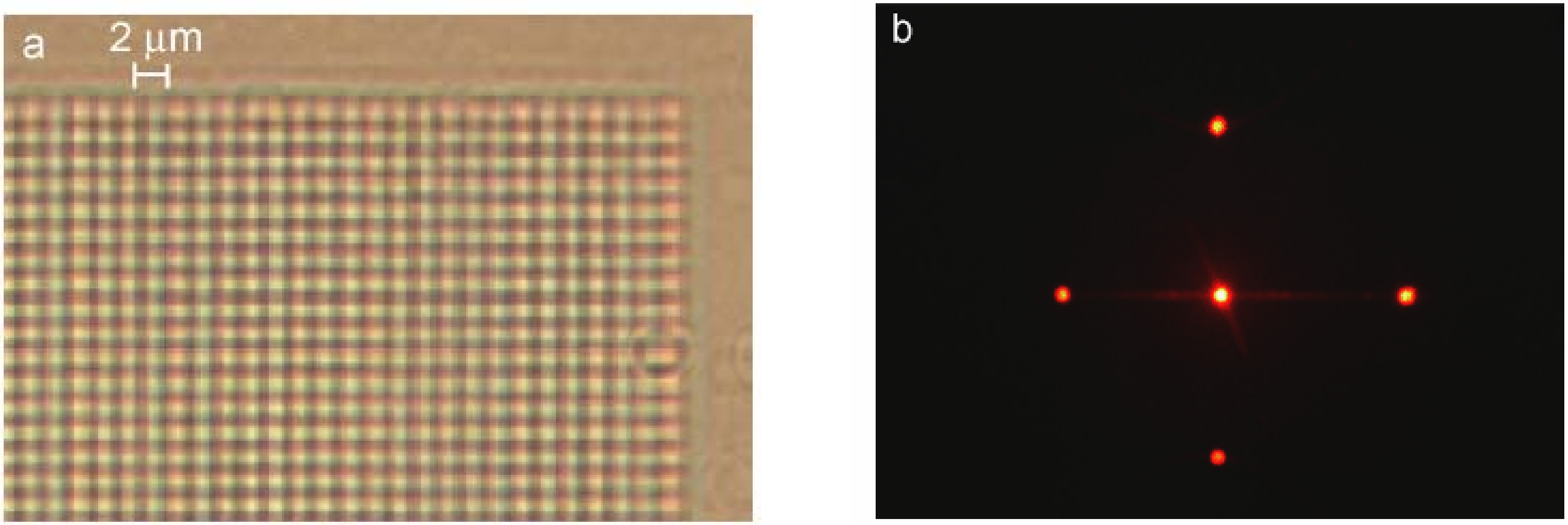


Fig. 4. Transmission mode microscope picture of the square lattice of air holes in $As_{35}S_{65}$ with a period of 0.8 μm and a hole diameter of 0.48 μm (a) and diffraction pattern at a wavelength of 633 nm at normal incidence (b).

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

Summary

Glasses, mainly some chalcogenide glasses, can be applied as highly sensitive resists with extraordinary resolution going down to nanometers size

both, positive and negative resists can be achieved

Easy to prepare large array films with controlable thickness, good adhesion to Si, SiO_2 , Si_3N_4 …, and strong resistance to HF, H_2SO_4 , H_3PO_4 , HCl…and or gasses as CF_4

direct structuring using high energy high intensity beam

3 D nanostructures can be fabricated in CHG using UVDLW and/or electron beam lithography down to 100 nm and 10 nm, respectively

Do you know now the answers?

- **What is lithography? What is glass?**

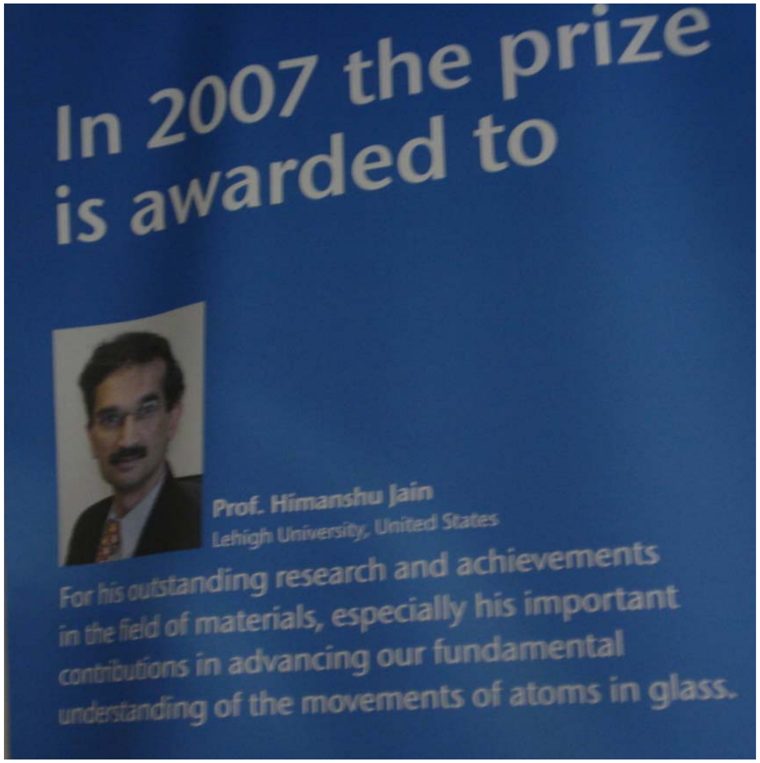
- **Can glass be photosensitive?**

- **Can glass be selectively etched/featured? If yes, how and what is the resolution limit?**

- **Can a glass be applied in lithographic process and vice versa can lithography be applied to structure glasses?**

And still something pleasant before I say you GOODBYE

Prof. Himanshu Jain – winner of Otto Schott Research Award – 2007
Director of IMI



- outstanding work towards advancing fundamental understanding of the movements of atoms inside glass
- research into unique light-induced phenomena in glass
- studies of the corrosion of glass in nuclear environments
- studies in the field of sensors, infrared optics, waveguides, photolithography, nanolithography and other photonic applications of glass

Thank you for your attention

Your feedback highly appreciated at:

Miroslav.Vlcek@upce.cz

or

MiroslavVlcek@yahoo.com

GOODBYE!!!