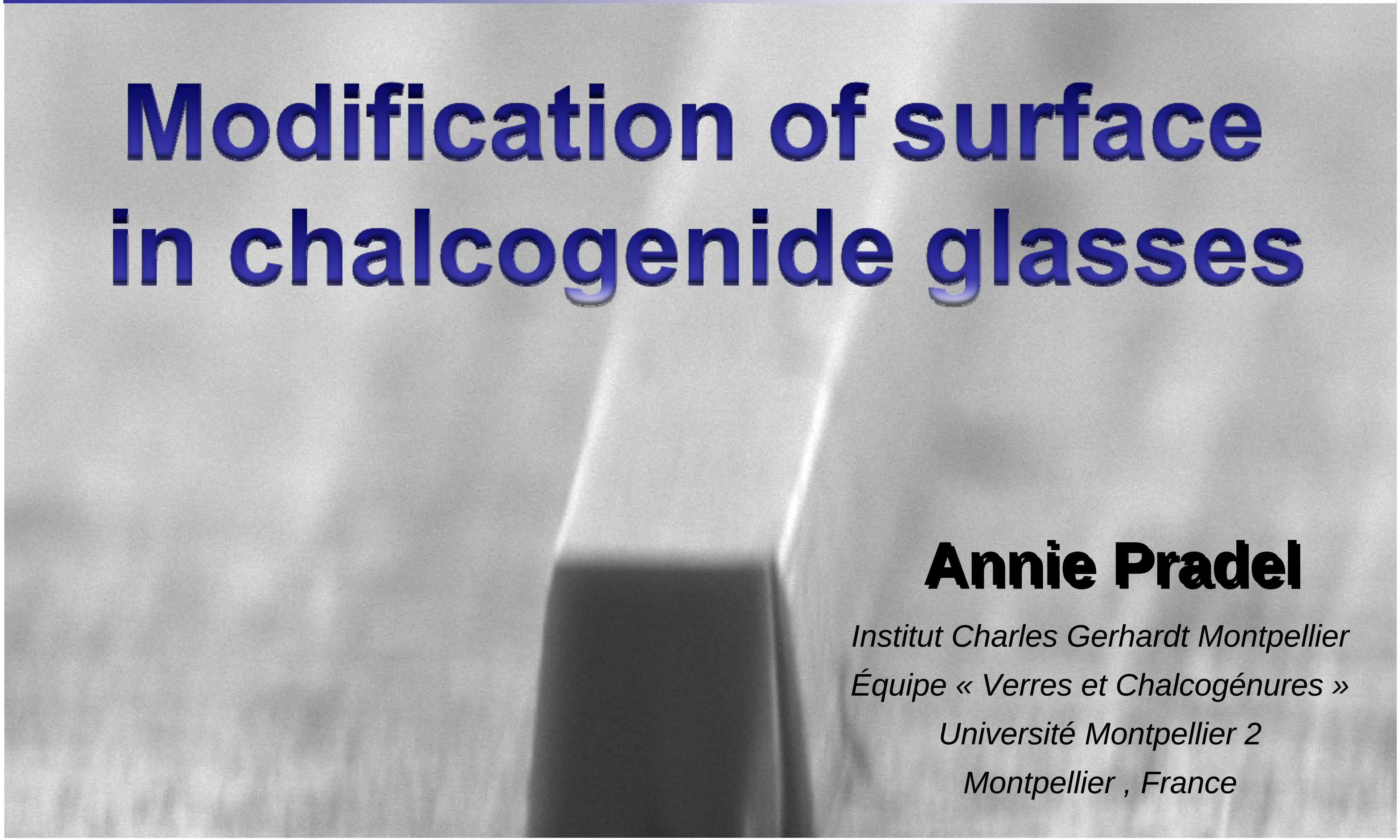

Modification of surface in chalcogenide glasses

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Montpellier , France

Chalcogenide glasses

Chalcogen homologous of oxide glasses

SiO_2 ; GeO_2 ➡ $SiS(e)_2$; $GeS(e)_2$

Ia	IIa	IIIb	IVb	Vb	VIb	VIIB	VIIIb			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns											
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Specific properties of chalcogenide glasses

Presence of S, Se, Te → ***polarisable environment (lone-pair-LP)***

Specific property of chalcogenide glasses compared to oxide ones

Semiconductor

As_2S_3 glass

$\sigma \sim 10^{-14}$ Scm^{-1}

$E_g \sim 2.15$ eV

Photoinduced phenomena

hν -> hole-electron pair

-> change in n

-> Ovshinsky effect

(amorphous state <-> crystalline state)

Large ion mobility

When doped with alkali, silver or copper ions,

Transparent in the IR

- Photoinduced phenomena
- Ion mobility

Diffusion under photons hν: Photoinduced phenomena

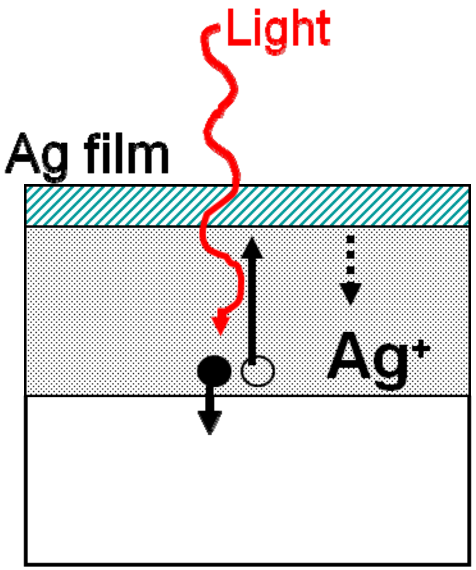
Photodissolution (« photodoping »)

Illumination of a chalcogenide film in contact with silver

⇒ Rapid penetration of the metal into the semiconductor (Kostyshin (1966))

Typical features:

- *Large amount of Ag can be dissolved 30-40 at%, and even 57% in GeS_3*
- *Rate of dissolution depends on chalcogenide composition (excess in chalcogen)*



***hν** close to band-gap energy*

Mechanism

- **Ionization of Ag**
  (semiconductor → presence of holes or electrons)
  $Ag + h^+ \rightarrow Ag^+$ $\qquad$ $Ag \rightarrow Ag^+ + e^-$

- **Reduction of chalcogenide**
  $2Ag + Se \rightarrow Ag_2Se$ $\Delta G^\circ_{298} \sim -25$ kJ/mol
  $4Ag + 2As_2Se_3 \rightarrow 2Ag_2Se + As_4Se_4$ $\Delta G^\circ_{298} \sim -12$ kJ/mol

Photo-enhanced solid state reaction

Application of photodissolution

- **Very sharp edges between doped and undoped regions**

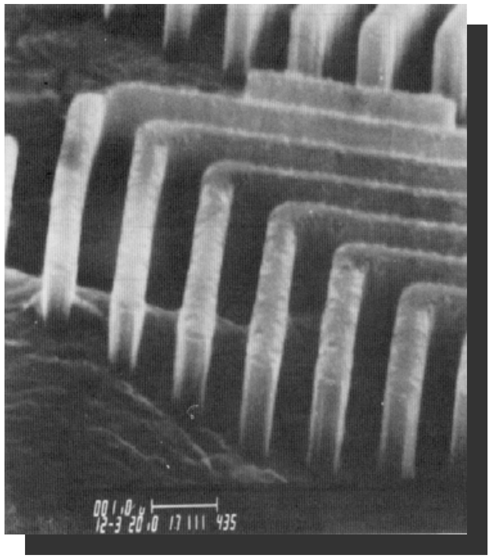
  Local creation of pairs « electron-hole » + small diffusion length of free carriers

  → ***Hardly any lateral diffusion***

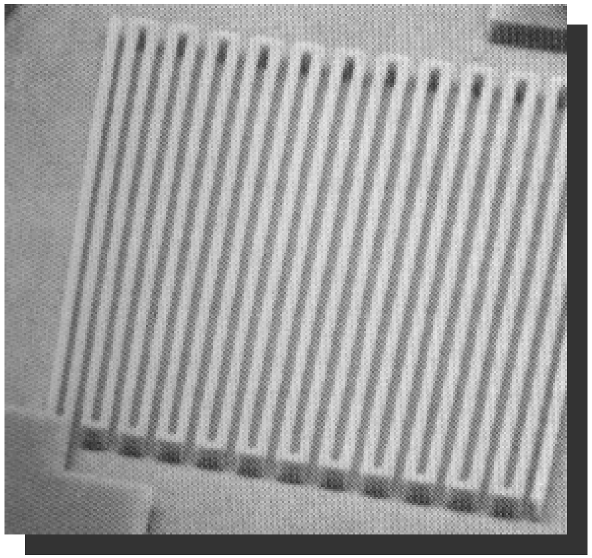
- **Solubility of doped region in alkaline solvents much reduced**

  → ***Local change in chemical composition***

photoresists



etched gratings



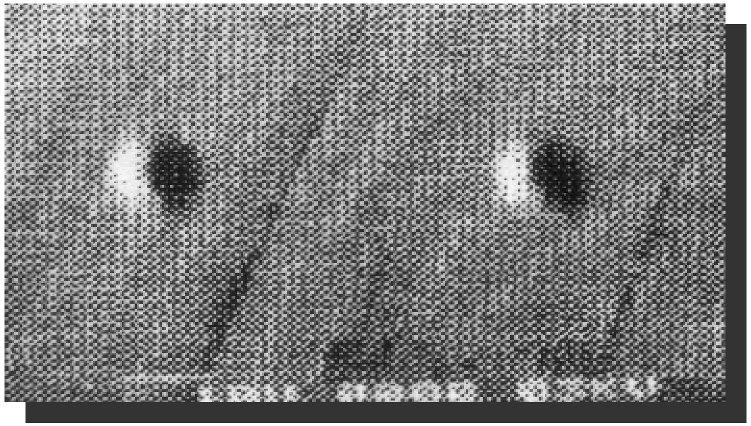
Photomigration – Photodeposition

Phenomenon observed in highly doped chalcogenide (Ag-Ge-S(e)), Ag-As-S(e))

Illumination

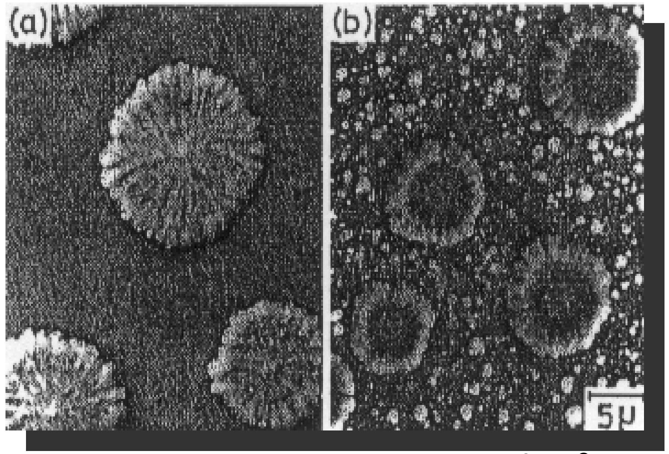
Lower silver content (x < 0.45)

increase in Ag density
in the illuminated part



Higher silver content ($Ag_{45}As_{15}S_{40}$)

precipitation of Ag



200mW/cm² 530mW/cm²

Small clusters or crystals
10nm in diameter and 1nm in thickness

Reversible process

Annealing → dissolution of the Ag clusters

Mechanism of photomigration-photodeposition

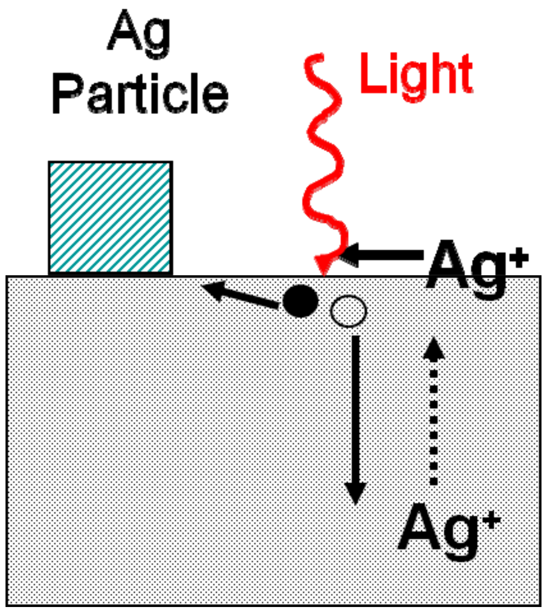
Point of view of physicist

Illumination

creation of pair « electron-hole »

$Ag^+ + e^- \rightarrow Ag$

h^+ moves away from illuminated spot



Point of view of chemist

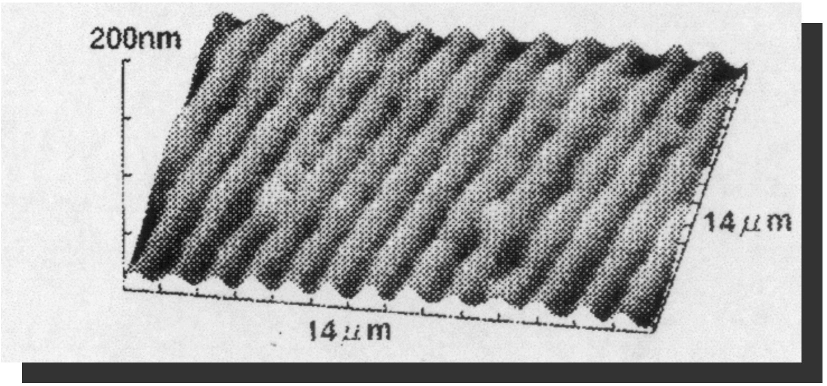
Photodecomposition = decomposition of an oversaturated Ag solid solution

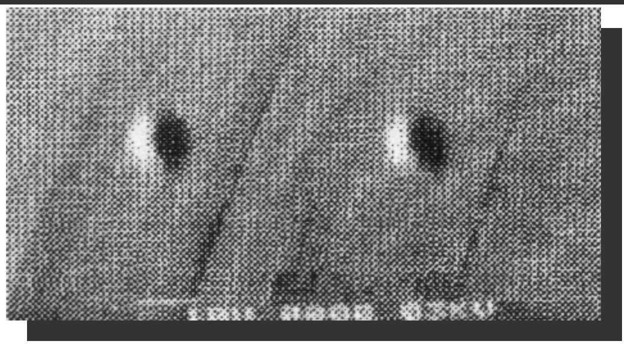
- *Under illumination the metastable system approaches equilibrium with excess Ag segregation.*
- *Annealing at higher temperature allows Ag to dissolve again in the solid solution.*

Application of photomigration-phodeposition

- **Increased reflectivity for Ag rich region**
- **Photoexpansion**

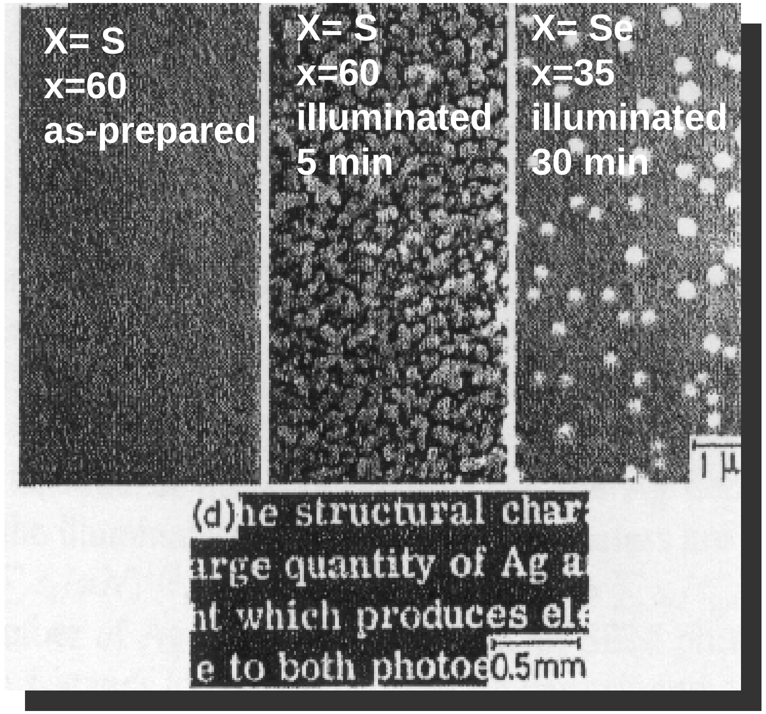
Gratings/ microlenses





Optical memories

$Ag_x(Ge_{0.3}X_{0.7})_{100-x}$, 110 mW/cm^2

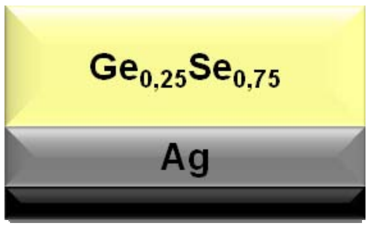


Au addition $\rightarrow$ increase in the photosensitivity of photodeposition by two orders of magnitude (Au clusters = nucleation centers for Ag)

Diffusion under E and hν: PMC memories

« Programmable Metallization Cell Memory Devices »

Ag_x/Ge_ySe_{1-y} multilayers

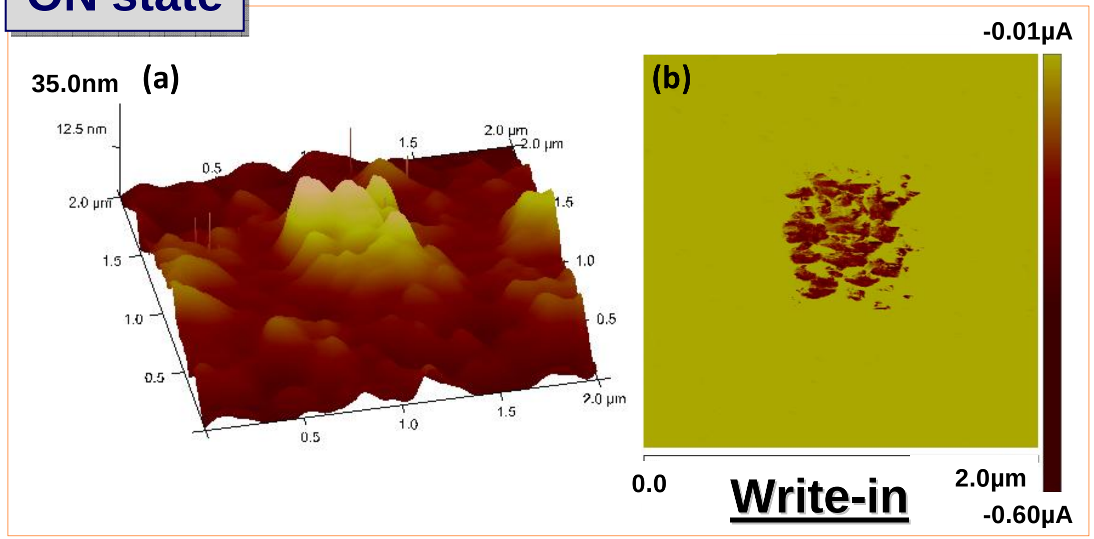


Conductive atomic force microscopy (C-AFM)

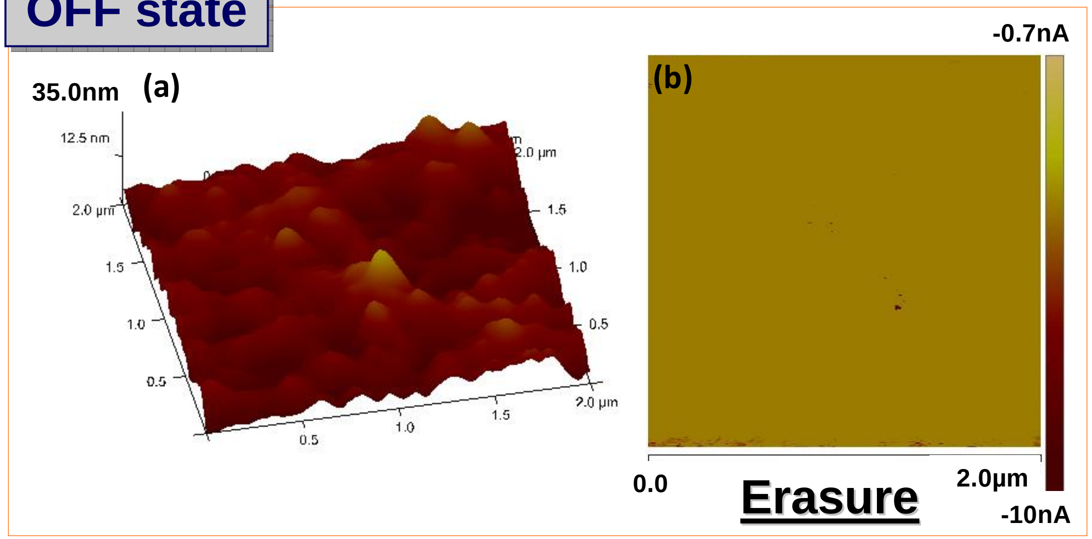
Write-in : Sweeping over 500x500 nm^2 and V_W = + 200 mV

Erasure : Sweeping over 500x500 nm^2 and V_E = - 250 mV

ON state

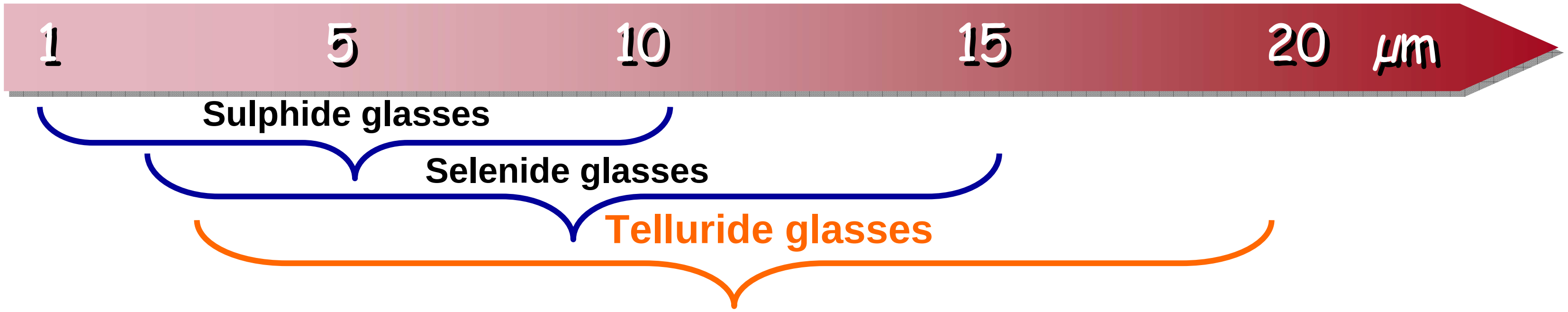


OFF state



- IR Transparency

IR Transparency



+ High refractive index
+ Easiness to put in film form

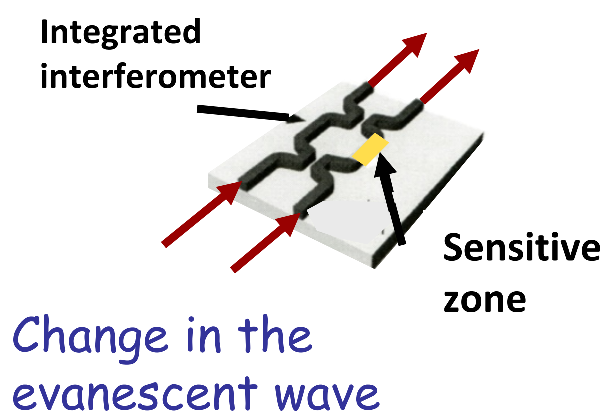
⇨ Promising materials for IR integrated optics

Feasibility of channel waveguides

Environmental metrology
Microsensors for detection of pollutant gases

Biology
Microsensors for biological monitoring

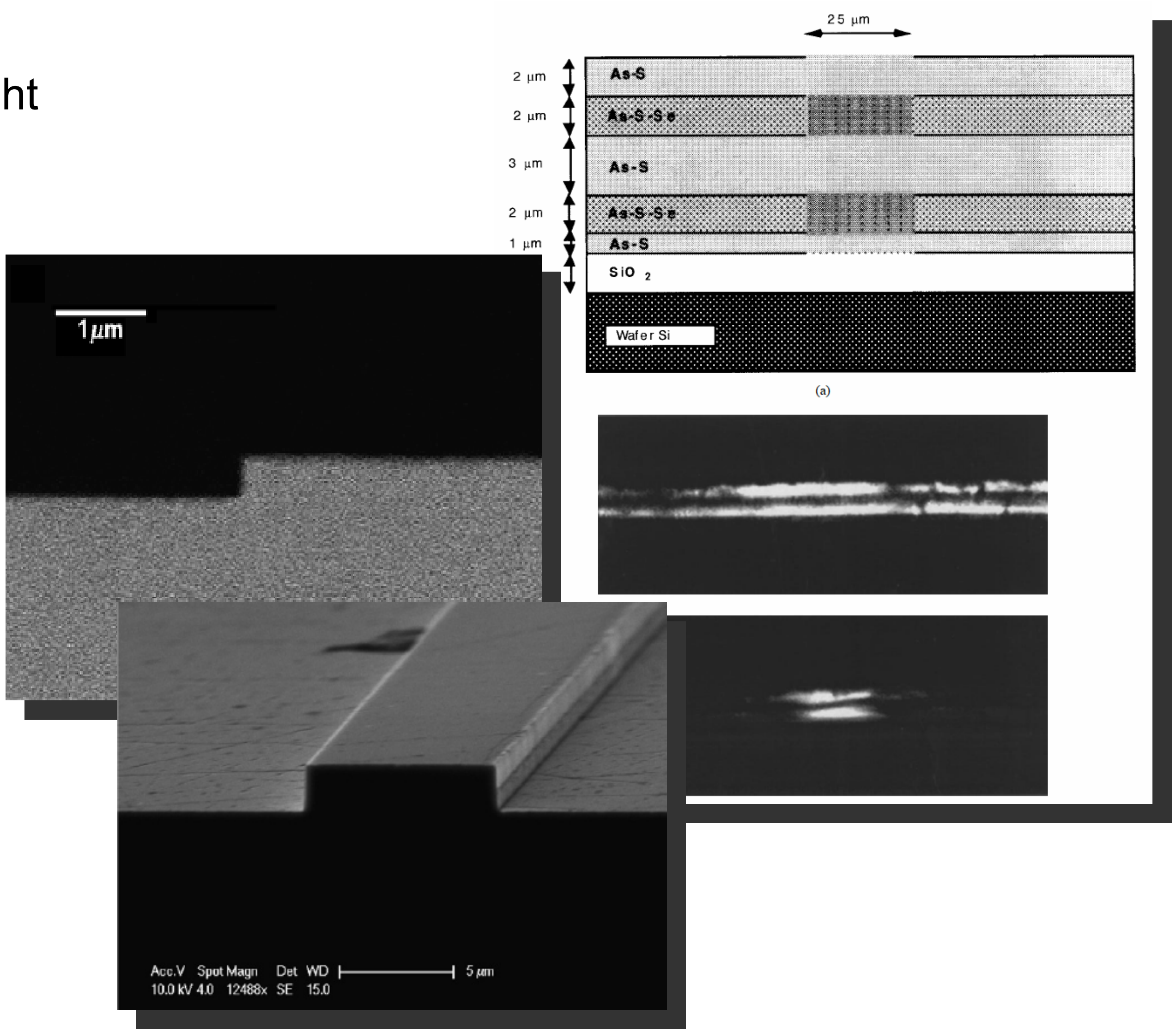
Optical amplification
Waveguide for active components



Channel waveguide development

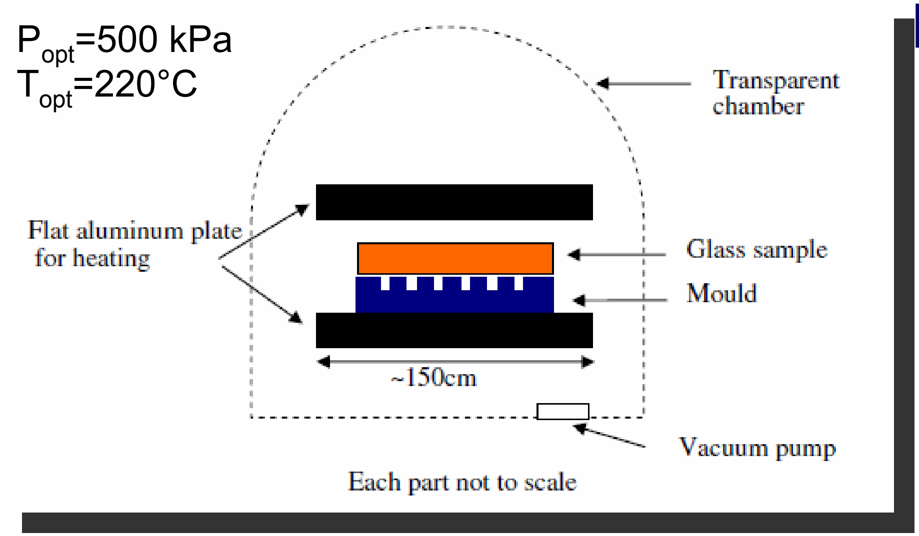
Lateral confinement of light

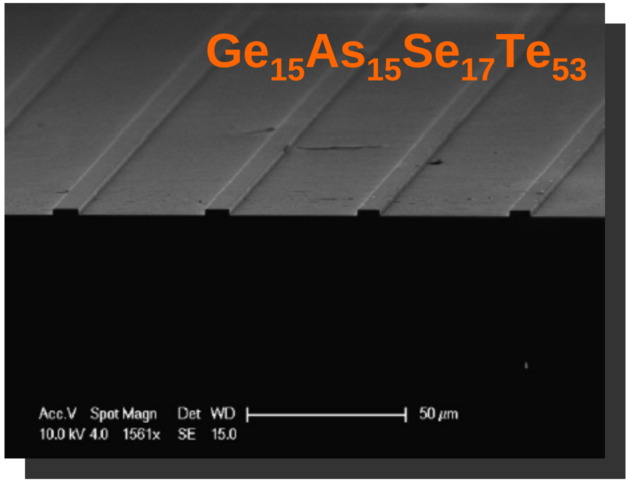
- **Laser writing**
- **Etching**
- **Embossing**



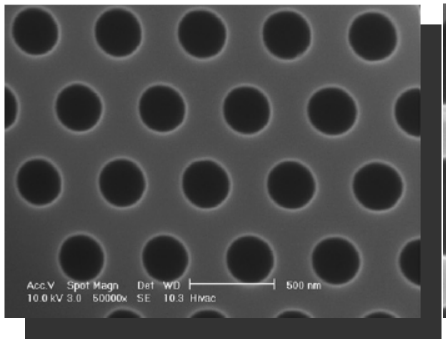
Channel waveguide development

Hot embossing

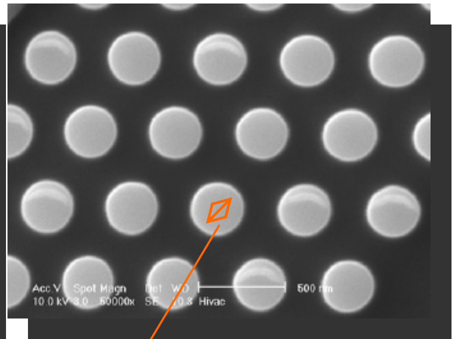




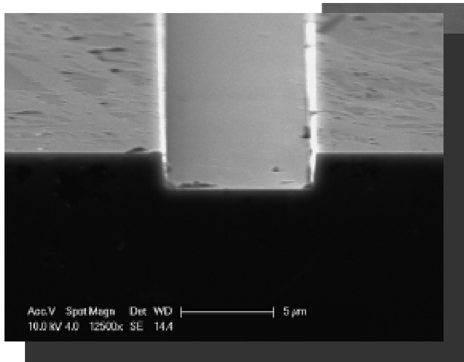
SOI mould



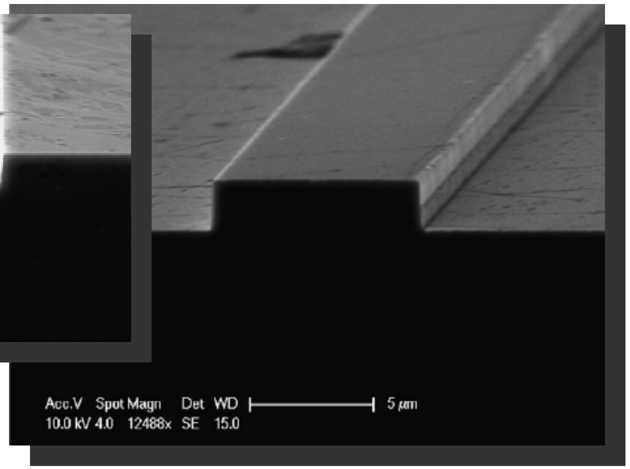
Accurate relief replication of the holes in the surface



300 nm



Si mould



Accurate relief replication of the silicon mould of a series of embossed ribs

W.J. Pan, D. Furniss, H. Rowe, C.A. Miller, A. Loni, P. Sewell, T.M. Benson, A.B. Seddon; J. Non-Cryst. Sol. 353 (2007) 1302–1306.

Channel waveguide development

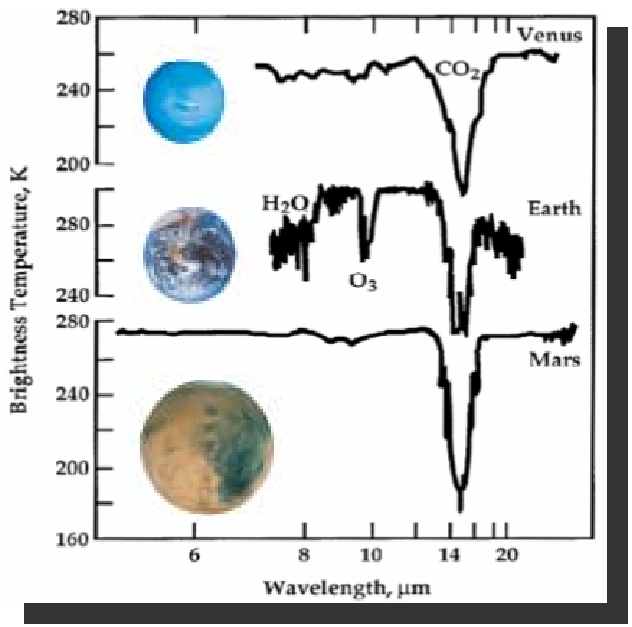
Components for spatial interferometer

Darwin mission:

Detection of exo-planetary systems

High contrast and very faint angular separation between an earth-like planet and its parent star:

mid and thermal infrared [6-20 µm]



Infrared signatures of:
- H_2O: 6µm
- O_3: 9µm
- CO_2: 16µm

Micro-components working between 6 and 20 µm

Channel waveguide development

Requirement

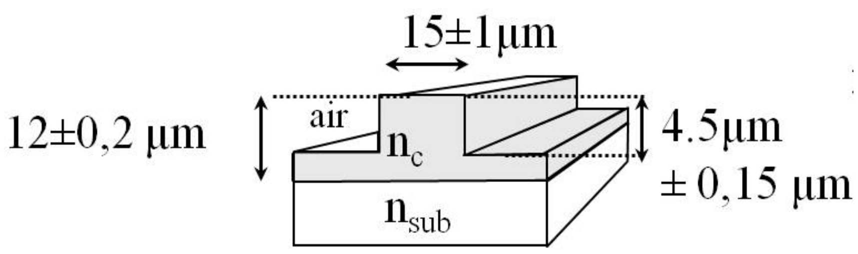
- Materials transparent between 6 – 20 µm
- Single mode waveguide

→ large dimension

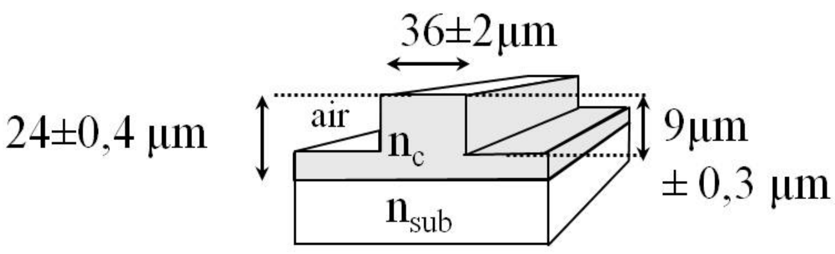
Design of component

- Spectral domain [6 – 20 µm] divided in two sub-bands
  [6 – 11 µm] and [10 – 20 µm]
- Considered structure with n_c = 3,44 ± 0,02: rib waveguide

[6 – 11 µm]



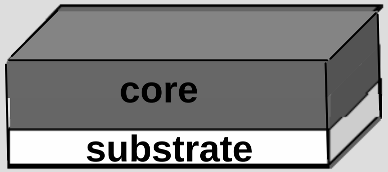
[10 – 20 µm]



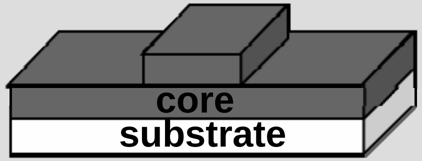
Walls with an angle comprised between 70 and 90 °

Channel waveguide development

Film deposition



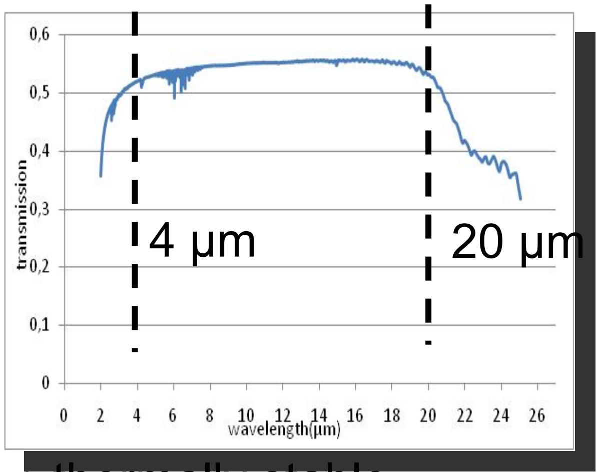
Film etching



Substrate composition

$Te_{75}Ge_{15}Ga_{10}$ bulk glass [X. Zhang (Rennes)]

- transmission between [4-20 µm]

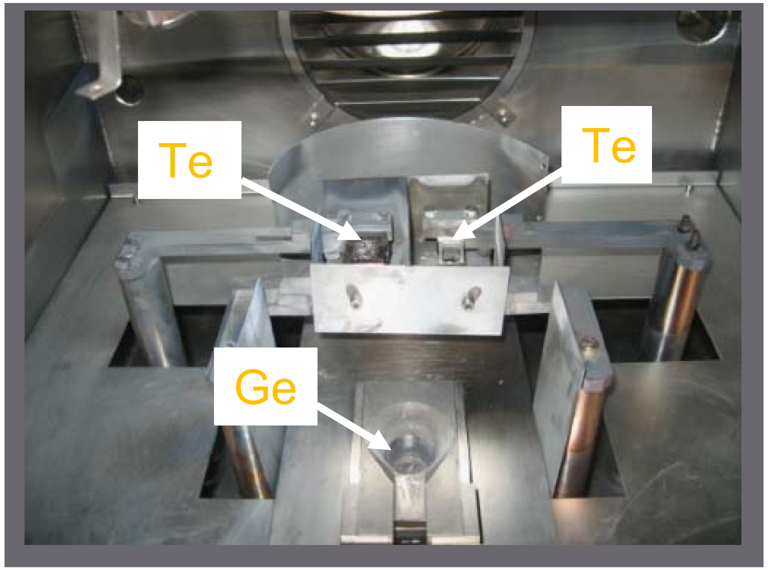


- thermally stable
- high refractive index

(at λ = 10.6 µm, $n_1 = 3.3990 \pm 0.0015$)

Core layer composition

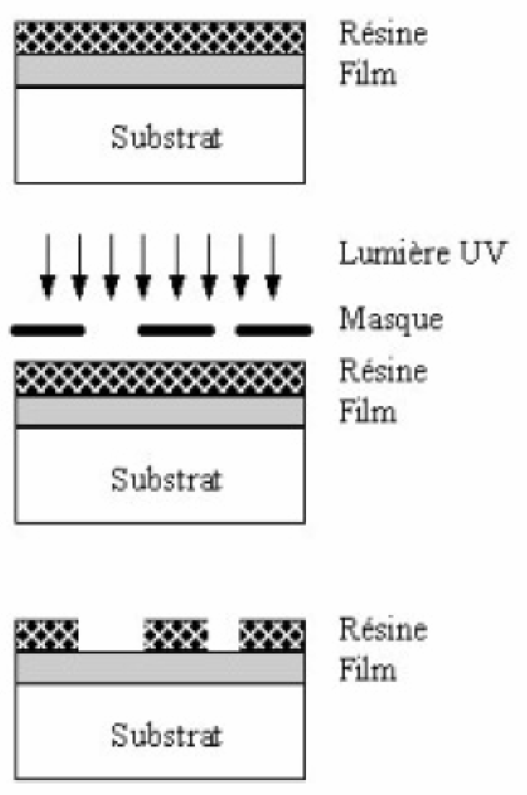
$Te_{82}Ge_{18}$ amorphous film



- **optimal composition: $n_2 = n_1 + 4.10^{-2}$**

Channel waveguide development

Photolithography



positive resist S.18.18
2 µm in thickness

Reactive ion etching

- ✓ CHF_3 → for chemical etching
- ✓ plasma → $F^{\bullet}$
- ✓ Reaction with Te and Ge

  TeF_6 , TeF_4 GeF_4 , GeF_2
- ✓ O_2 → enhancement of $F^{\bullet}$

Highly selective

Increase in etching rate ***but isotrope***

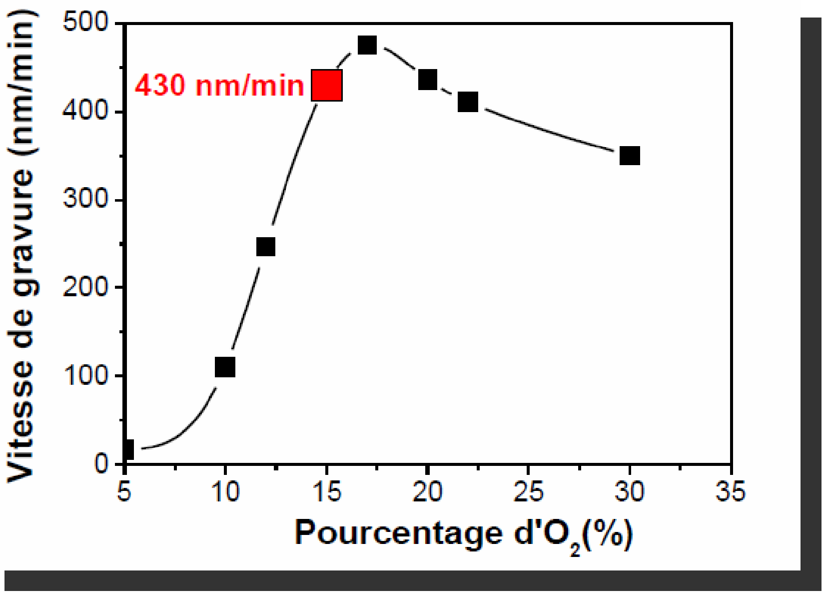
- ✓ Ar → for physical etching

Anisotrope ***but non selective***

Channel waveguide development

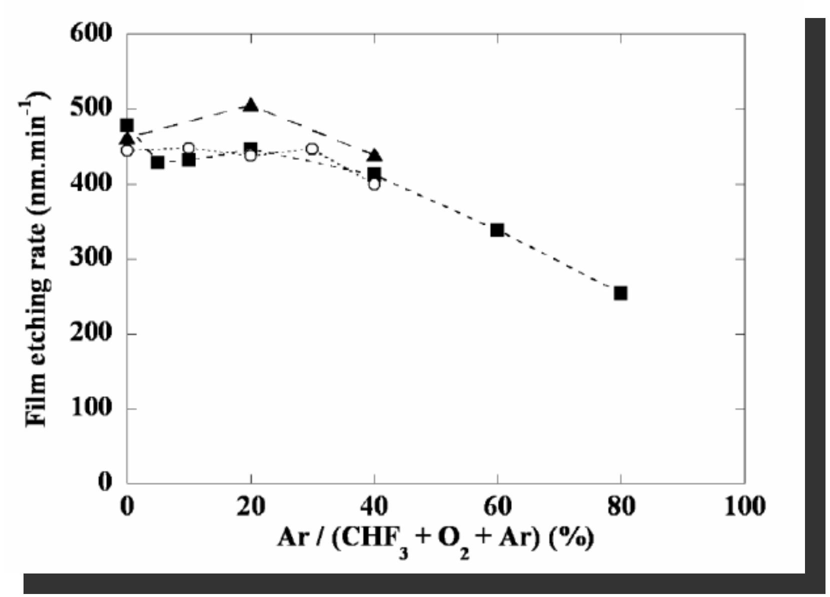
Optimization of etching gas

O_2 %

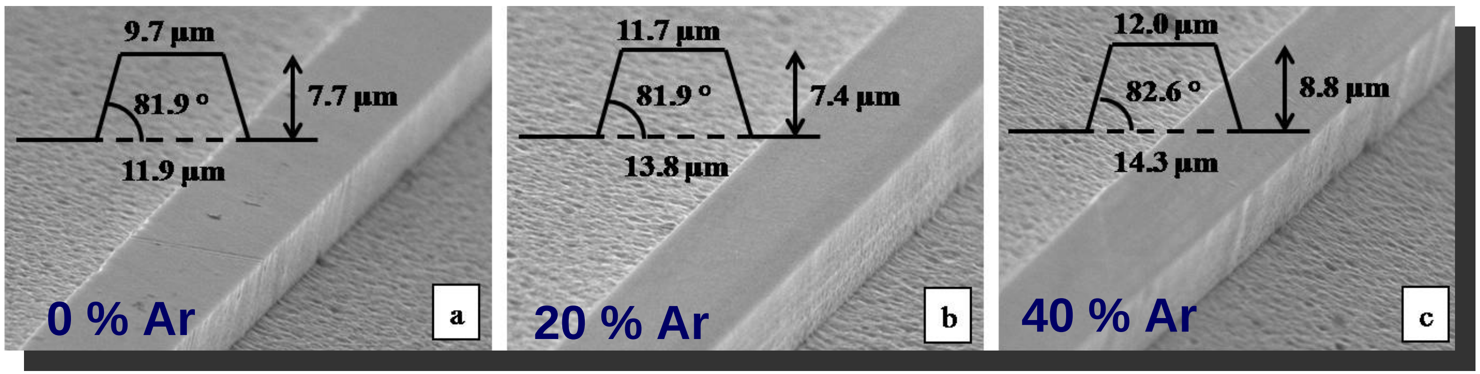


But surface contamination

Ar %



Poor impact but improve rib walls



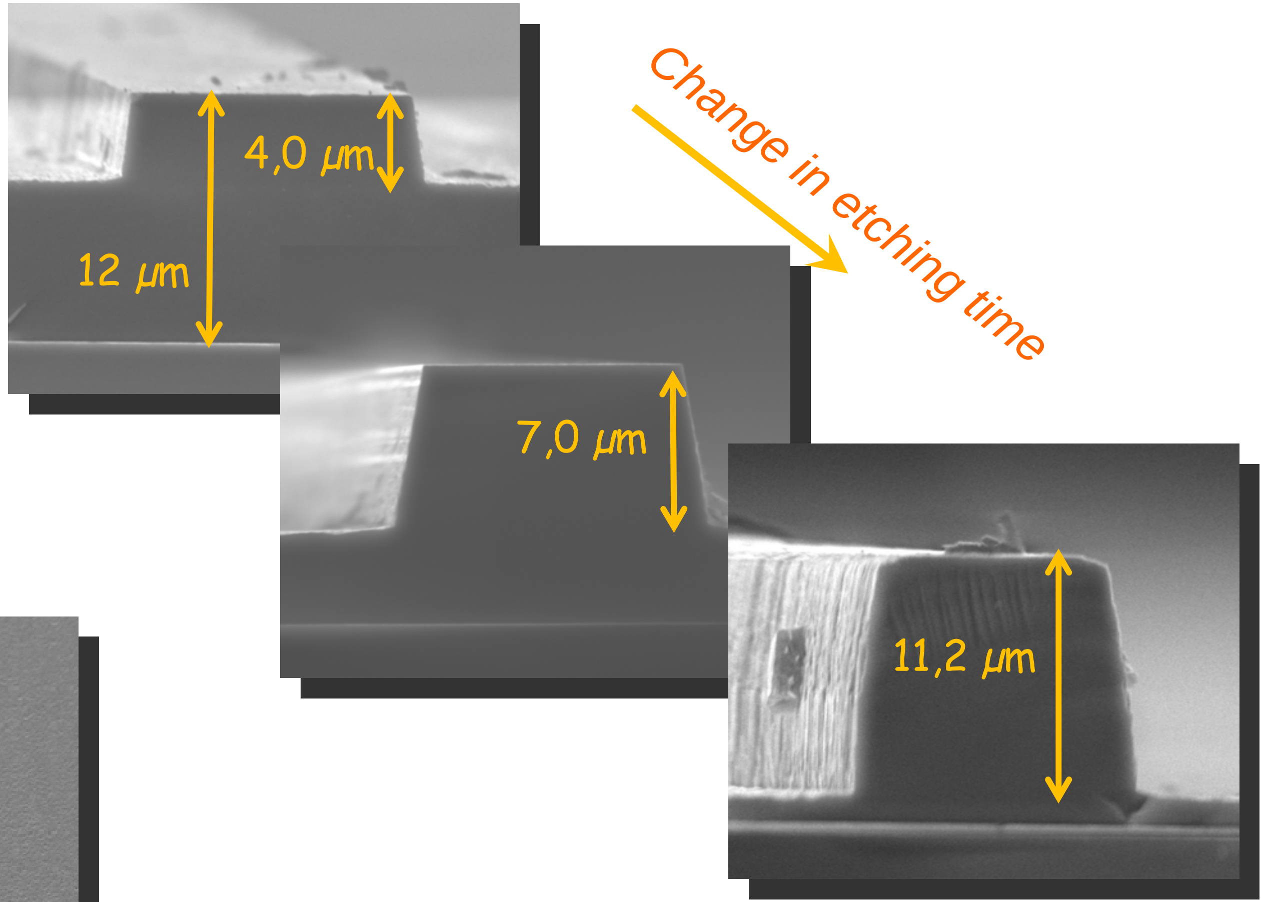
Channel waveguide development

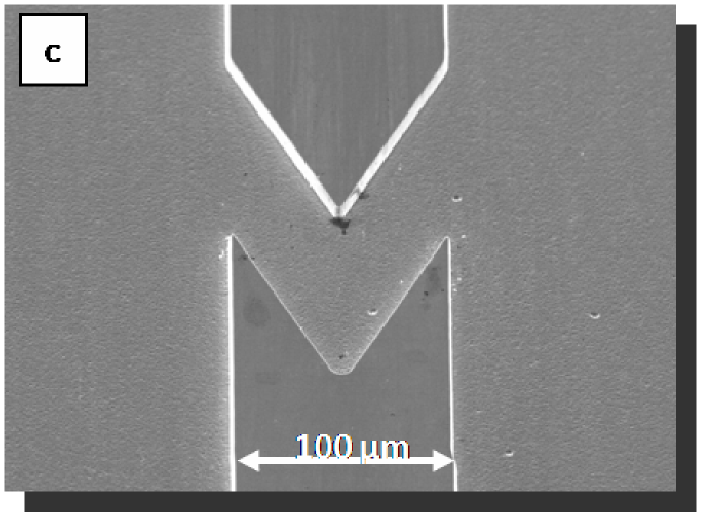
- **Reactive ion etching with optimized gas mixture**

Optimized $CHF_3/O_2/Ar$ ratio
= 59.5/10.5/30

CHF_3 / O_2 = 85 / 15

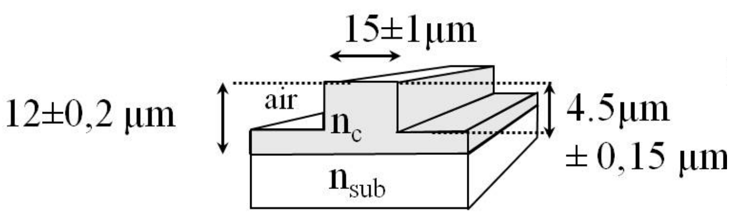
% Ar = 20

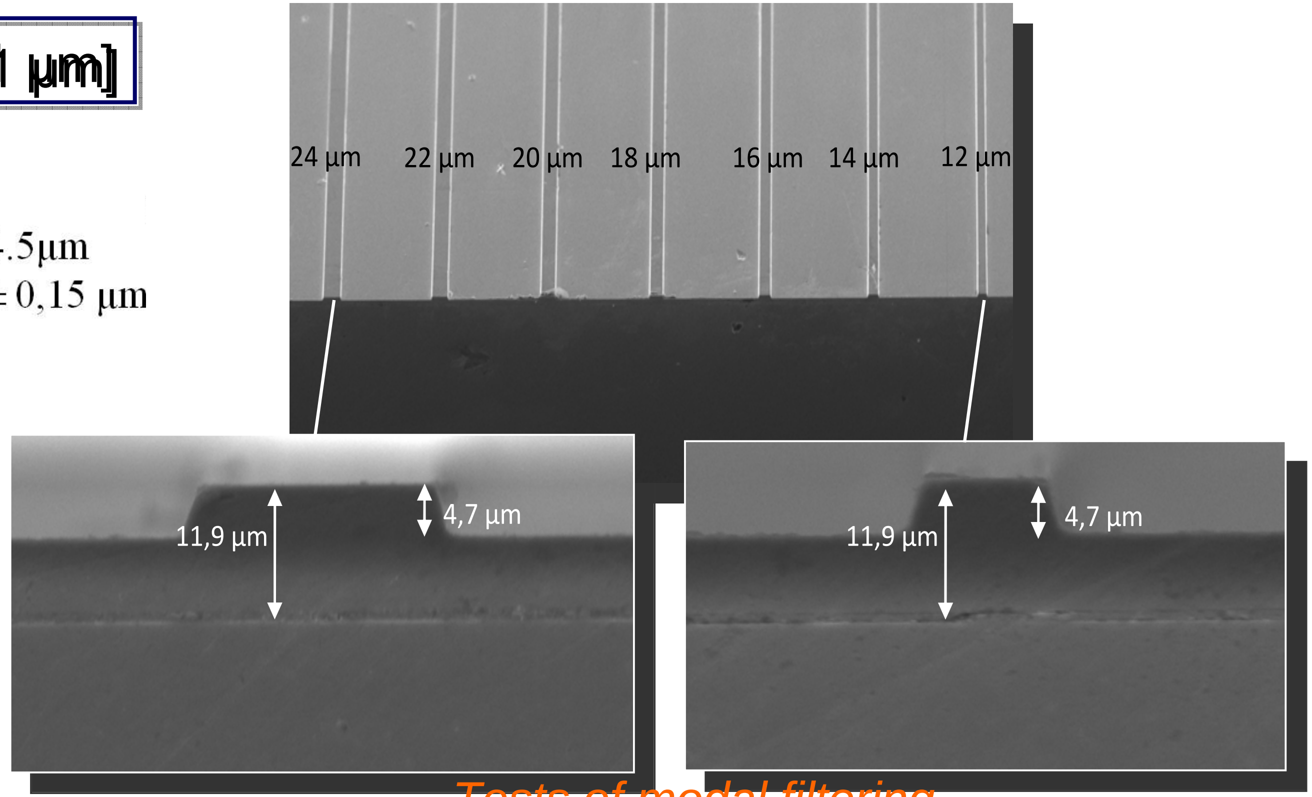




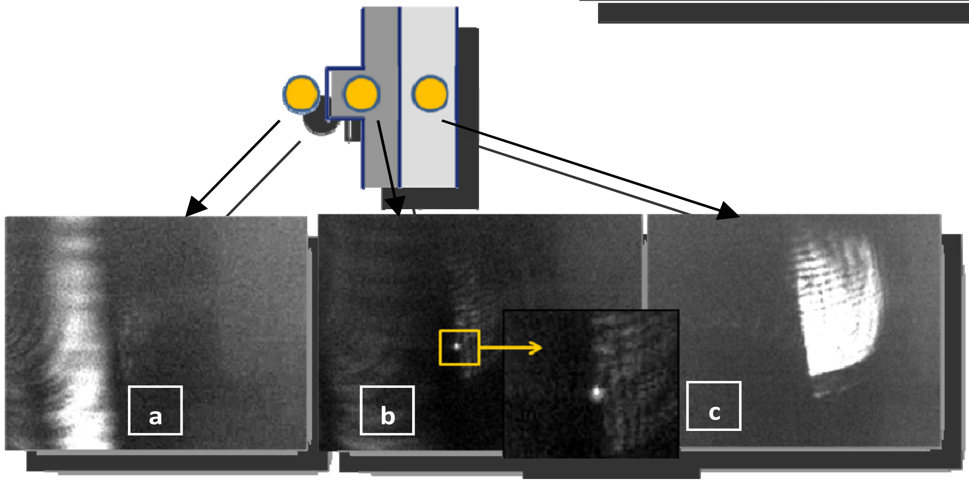
Channel waveguide development

Rib waveguides [6 – 11 µm]

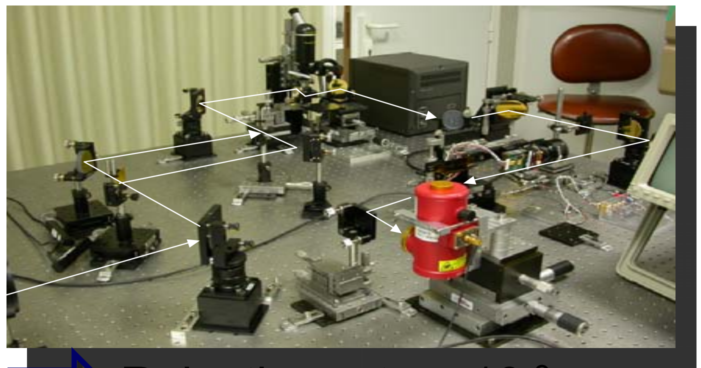




Tests at 10,6 µm



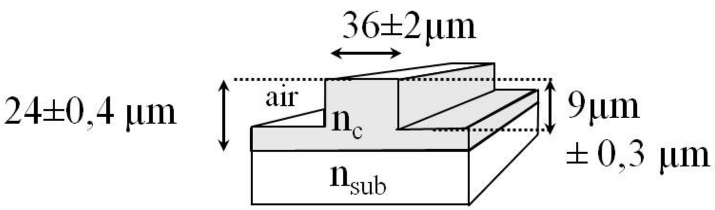
Tests of modal filtering

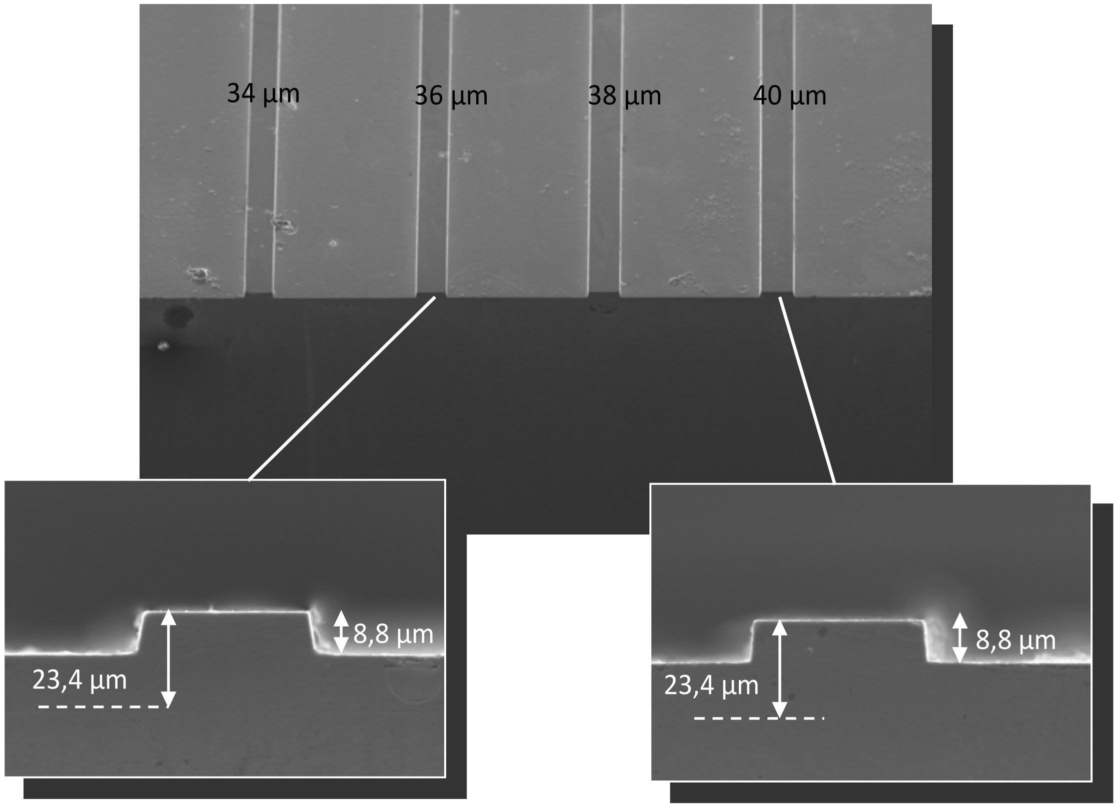


Rejection rate ~ 10^{-3}

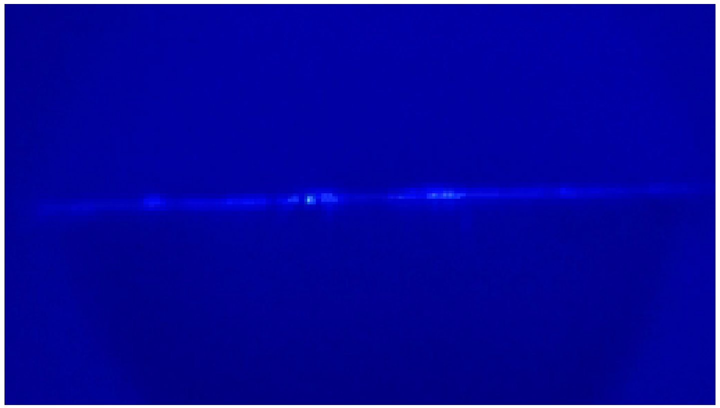
Channel waveguide development

Rib waveguides [10 – 20 µm]





Tests carried out in spectral region [1,5 – 5,5 µm]



Conclusion

Surface modification

- Use of intrinsic properties of chalcogenide

  (**photoinduced phenomenon + ion mobility**)

- Use of conventional techniques (**hot embossing, etching**)

  Development of components based on intrinsic property of chalcogenide (IR transparency)

Acknowledgments

My co-workers at ICGM Montpellier

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For C-AFM measurements:

M. Ramonda (*LMCP, Montpellier, France*)

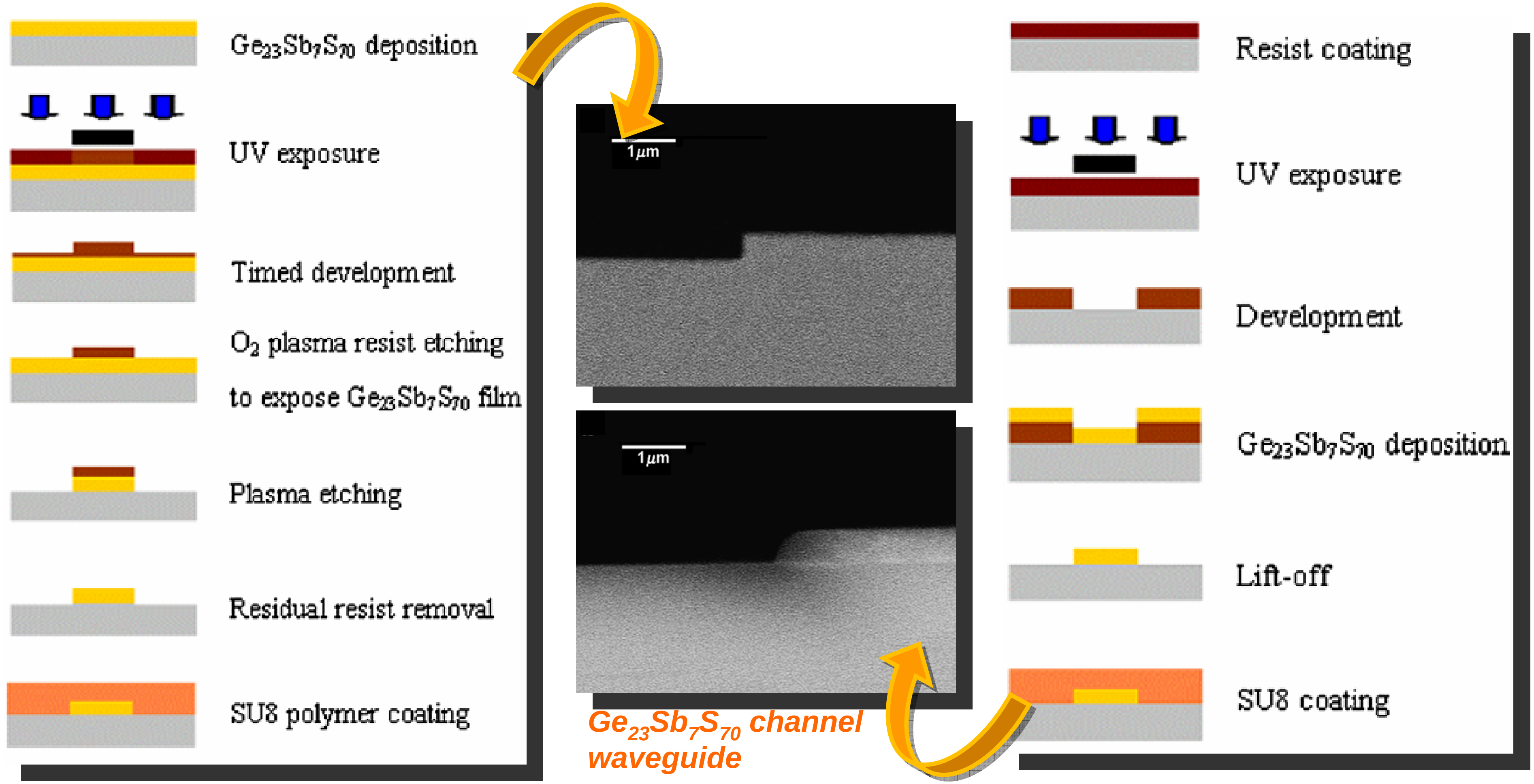
For contribution in the development and characterization of waveguides

M. Barillot (*Thalès Alenia Space, Cannes, France*), **X. Zhang** (*LVC, Rennes, France*), **G. Parent** (*LEMTA, Nancy, France*), **J.E. Broquin** (*IMEP, Grenoble, France*)

For financial support: European Space Agency (Project IODA2)

Fabrication de guides d'onde: Gravure

Waveguide fabrication by plasma etching ***Waveguide fabrication by lift-off***



J. Hu, V. Tarasov, N. Carlie, L. Petit, A. Agarwal, K. Richardson, L. Kimerling, Optical Materials 30 (2008) 1560–1566.