The Abdus Salam International Centre for Theoretical Physics

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Preparatory School to the Winter College on Optics and the Winter College on Optics: Advances in Nano-Optics and Plasmonics

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Applications to gas sensing

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BLOCH SURFACE WAVES ON PHOTONIC CRYSTALS

APPLICATIONS TO GAS SENSING AND BIOPHOTONICS

SAPIENZA Università di Roma
Department of Basic and Applied Sciences for Engineering
Molecular Photonics Laboratory

Francesco Michelotti

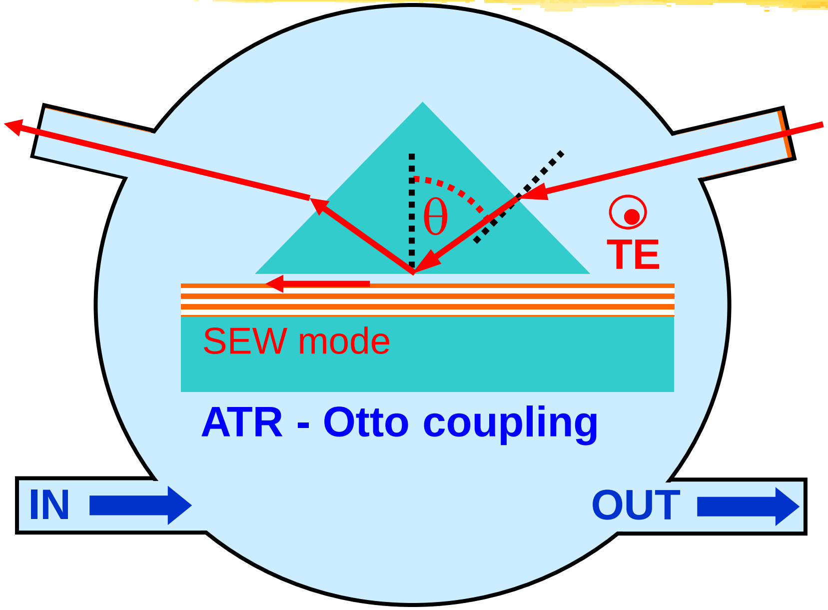
International Centre for Theoretical Physics, Trieste, February 2010

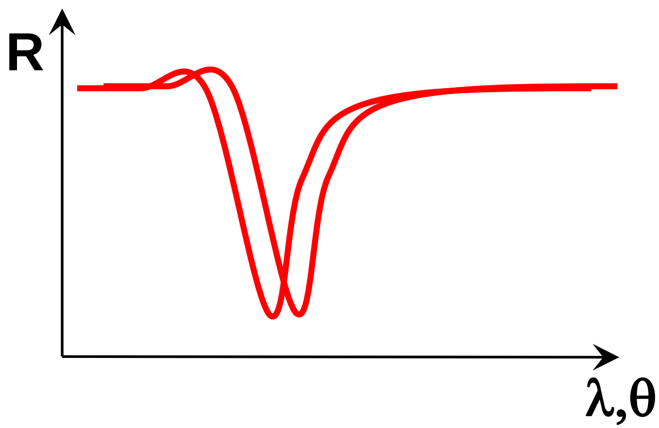
Lecture 3

Applications of BSW to gas sensing

(Experiments)

Issues on gas sensing with BSW





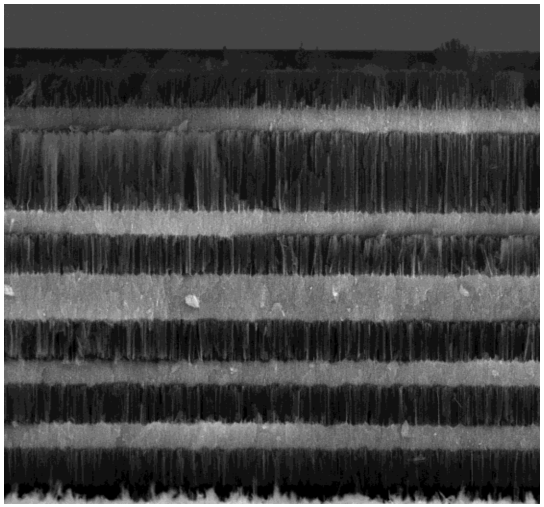
- The refractive index change due to exposition to a gas is not suffiently large to be detected by a BSW (and by a SPP)

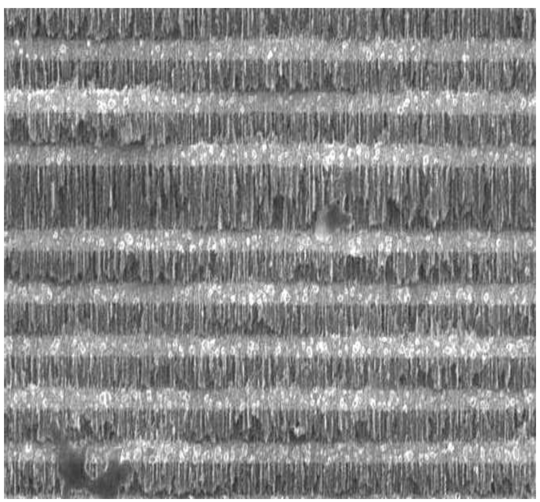
- Some amplification mechanism is needed

  Chemical → The gas modifies the 1DPC materials, giving rise to refractive index changes and detection

  Physical → The 1DPC modifies the gas phase (for example from vapour to liquid)

Porous silicon as a good material for gas sensing with BSW



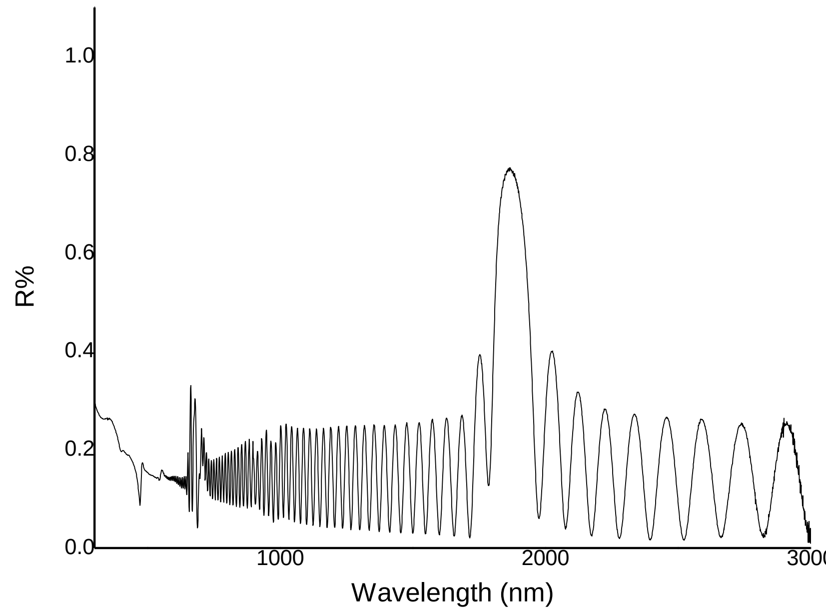


Porous silicon obtained by electro-chemical etching is a good candidate for BSW gas sensing.

- Stacks composed by layers with different porosity and refractive index can be etched in the same silicon wafer
- Very good definition of the layers thickness and refractive index
- Extremely large effective area (up to 800m^2/cm^3)
- Reactivity of the surface
- Porous structure modifies the vapour tension and forces condensation from gas to liquid phase

Porous silicon as a good material for gas sensing with BSW

- Electrochemical etching in HF:$H_2$0: C_2H_5OH starting from highly B-doped p+ type Si(100) with 7mΩ·cm
- The etching current density determines the porosity and the refractive index of the layers
- Etching of multilayers can be accomplished by modulating the current density either stepwise (discrete filters) or continuously (rugate filters)



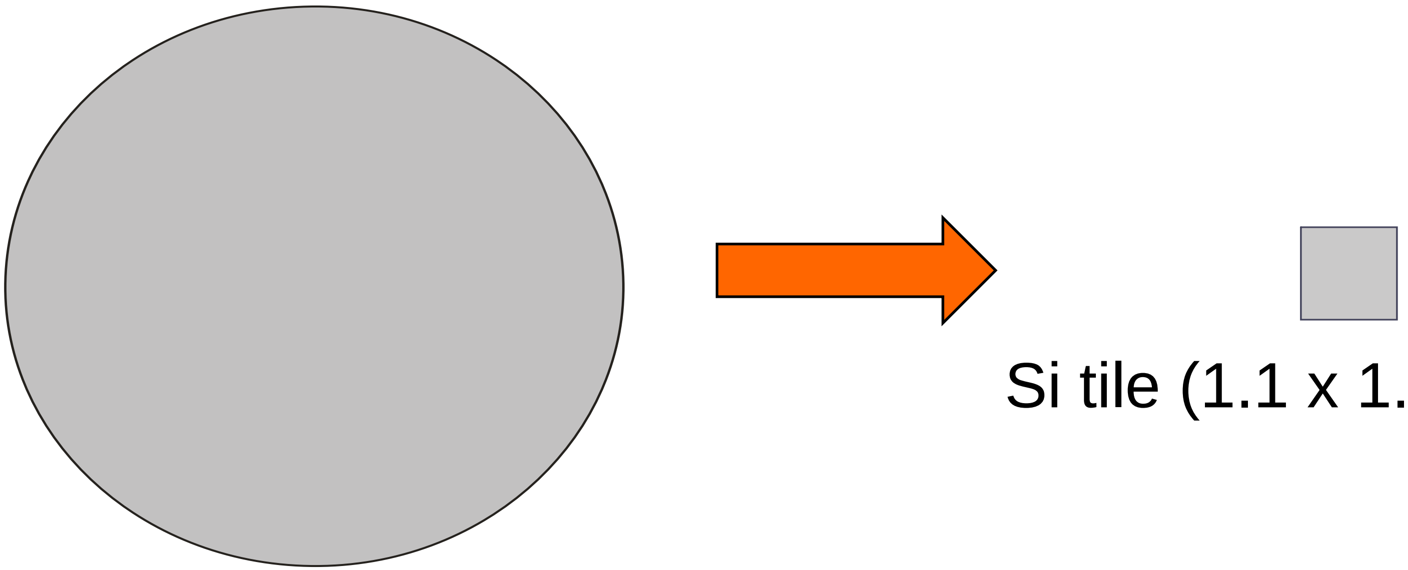
Bragg Mirror
25 periods of HL refractive index pairs
Current: 30mA-20mA; t etch : 10.11s - 11.66s, T=-24.8°C.

Porous silicon preparation

The morphology of PSi structures depends on some factors:

- Si doping type (p or n) and doping concentration
- Composition and concentration of the solution
- Temperature

Porous silicon preparation



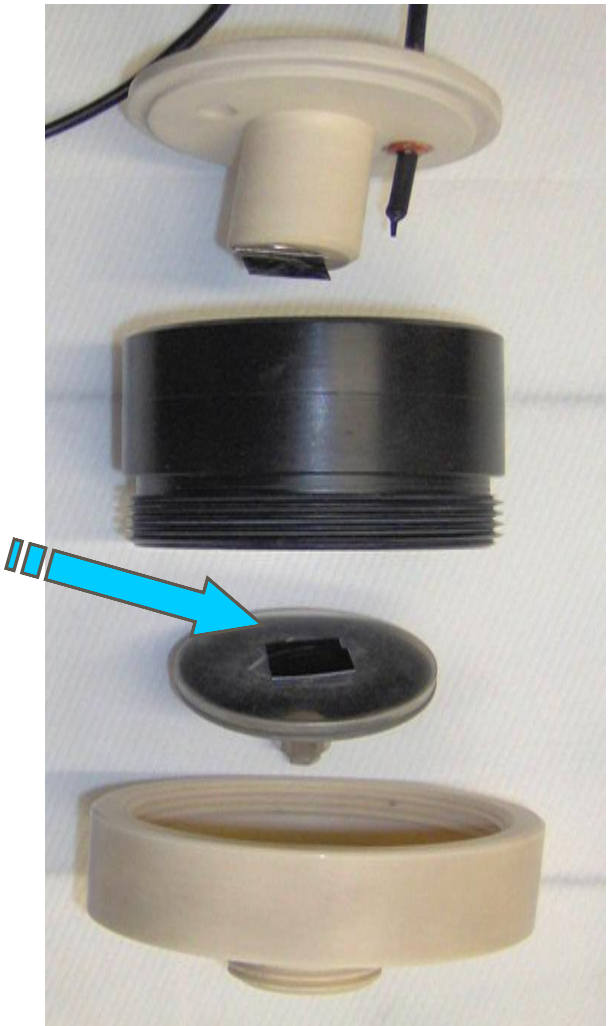
Si tile (1.1 x 1.1cm^2)

p^+ Si <100> wafer

resistivity: < 7 mΩ cm,

[B] $\cong 3\times10^{19}$ atoms/cm^3

Porous silicon preparation

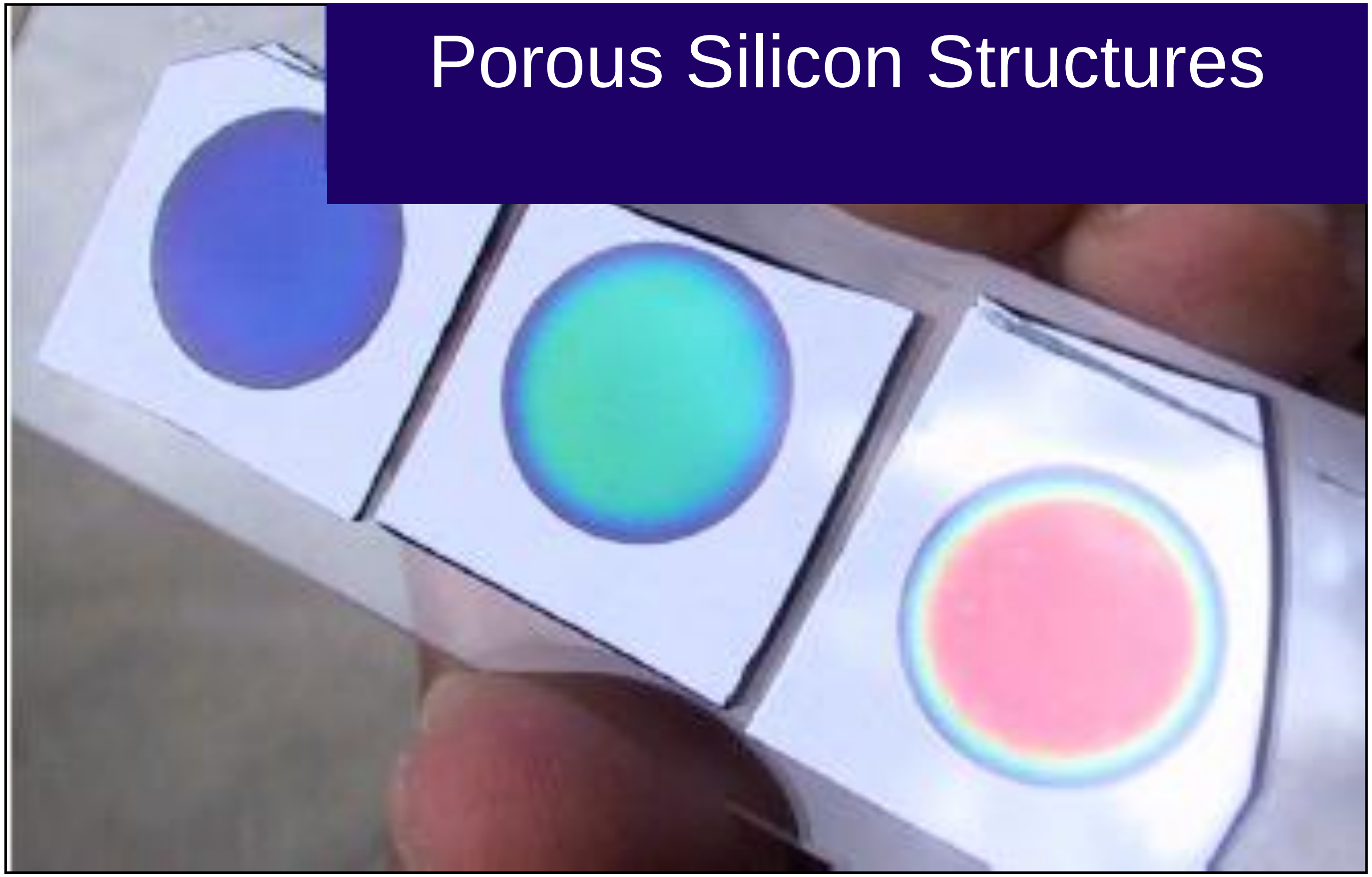


The electro-chemical cell is made out of a material resistant to HF.

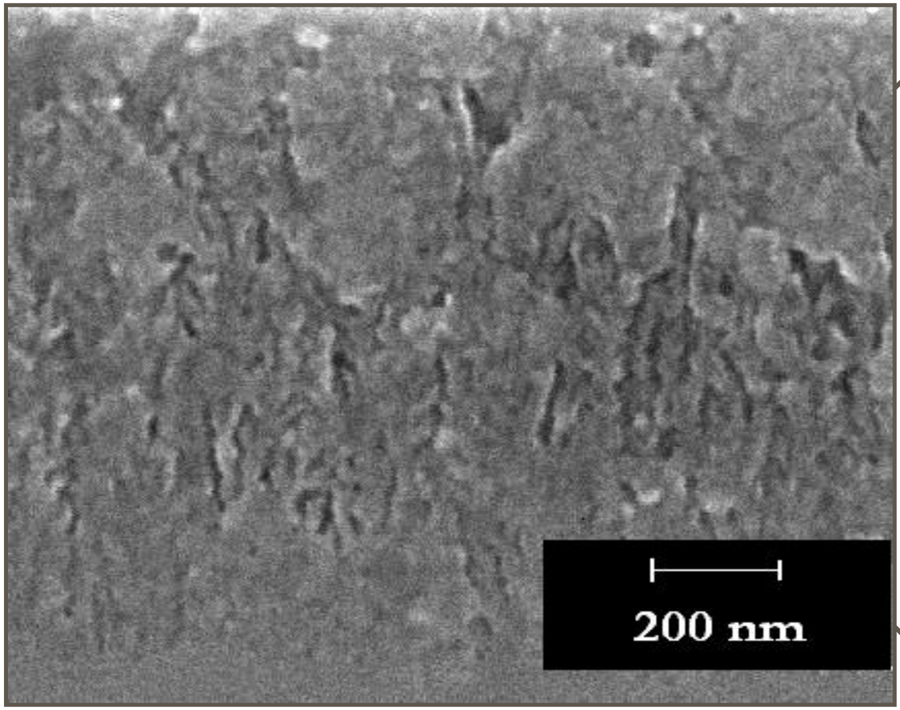
The cathod is a platinum electrode and the anode is the silicon wafer itself.

The solution composition is: [HF] 18%, [H2O] 18%, [C2H5OH] 64%.

Porous silicon preparation

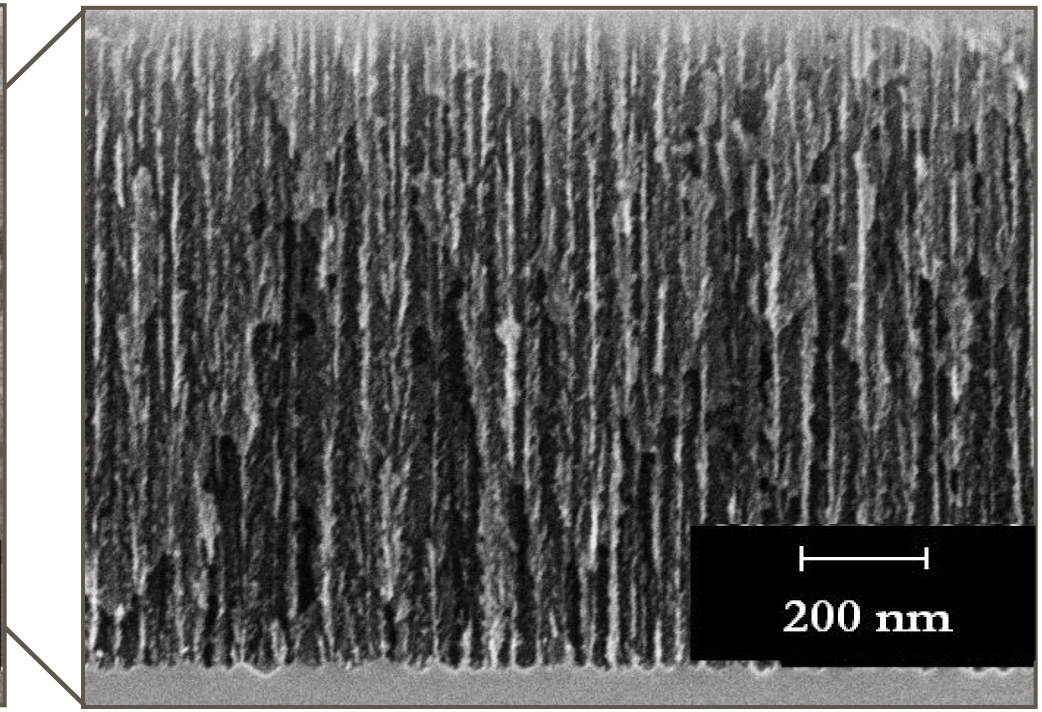


Porous silicon preparation – Single film



SEM single film

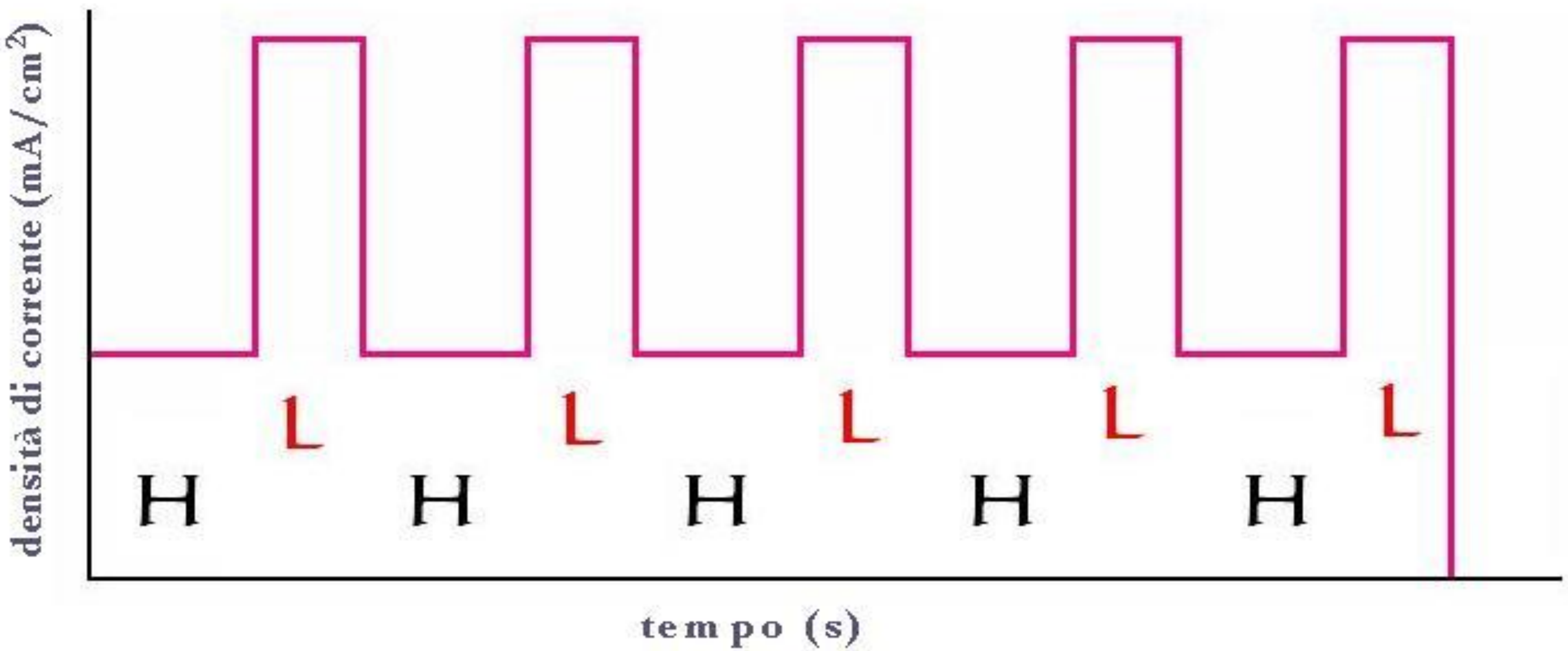
low porosity



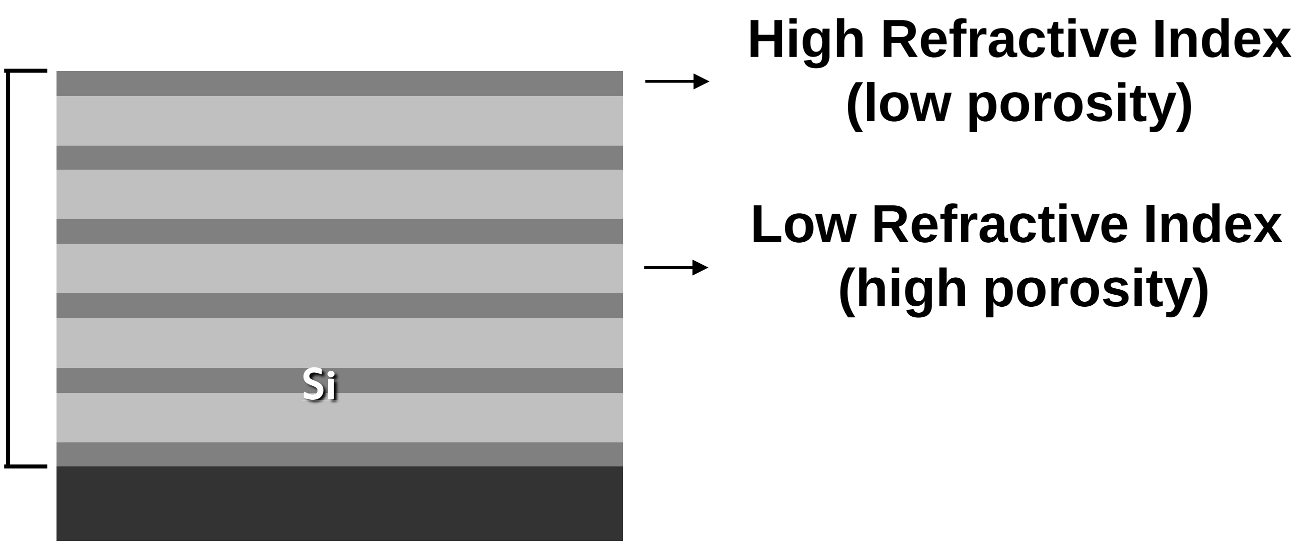
SEM single film

high porosity

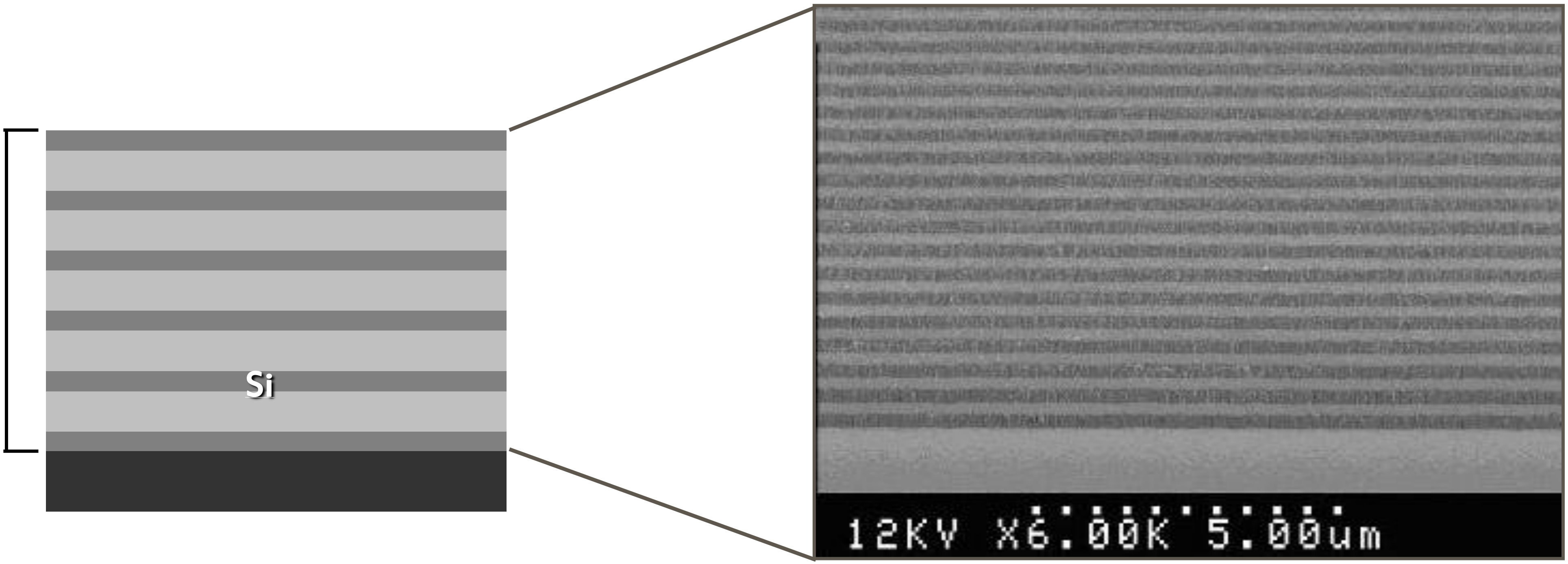
Porous silicon preparation – Multilayer



Porous silicon preparation – Multilayer



Porous silicon preparation – Multilayer



SEM

Porous silicon as a good material for gas sensing with BSW

Porous silicon can:

- Change electrical or optical properties due to the presence of liquids or gases or even solids (CH_3OH, NH_3, NO_2)

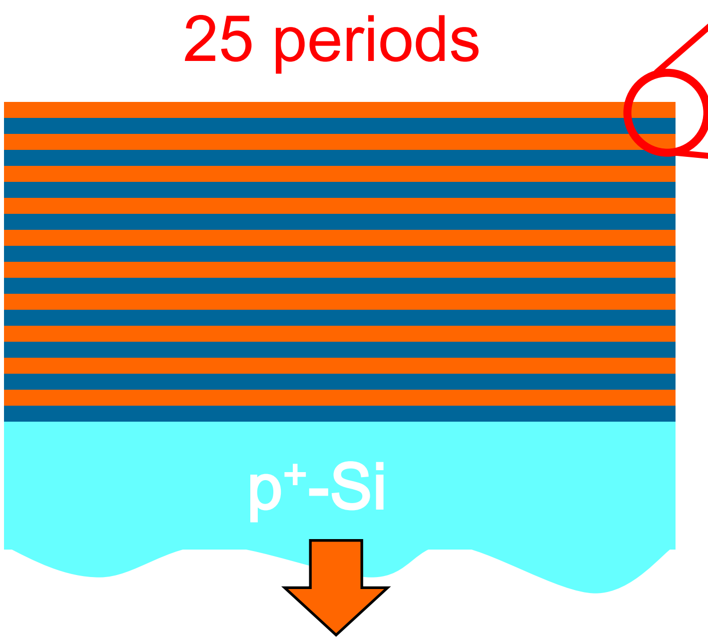
  E. Garrone, F. Geobaldo, P. Rivolo, G. Amato, L. Boarino, M. chiesa, E. Giamello, R. Gobetto, P. Ugliengo and A. Viale, Adv. Mater. 17, 528 (2005)

- Force gas vapours phase transition to the liquid phase by capillarity condensation

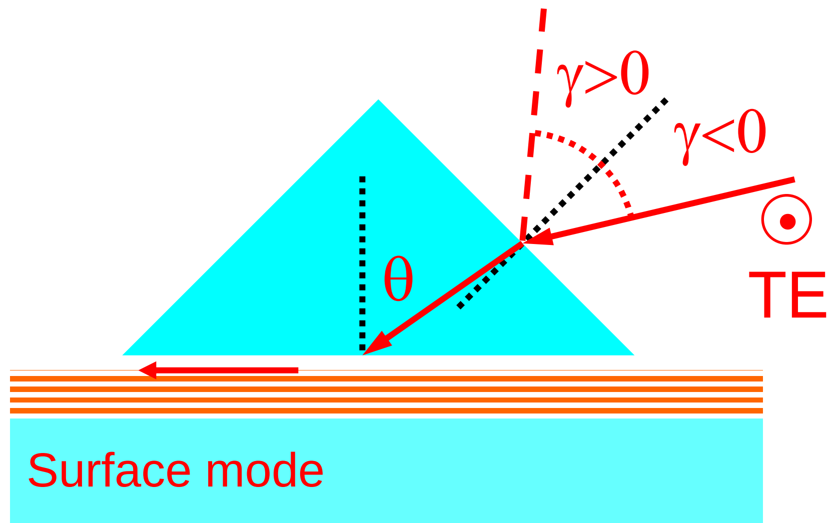
  S. Zangooie, R. Bjorklund, H. Arwin, Sensors and Actuators B, 43, 168 (1999)

Porous Silicon Multilayer – 25 periods

L	t=294nm n=1.75 @ λ=1530nm
H	t=240nm n=2.23 @ λ=1530nm

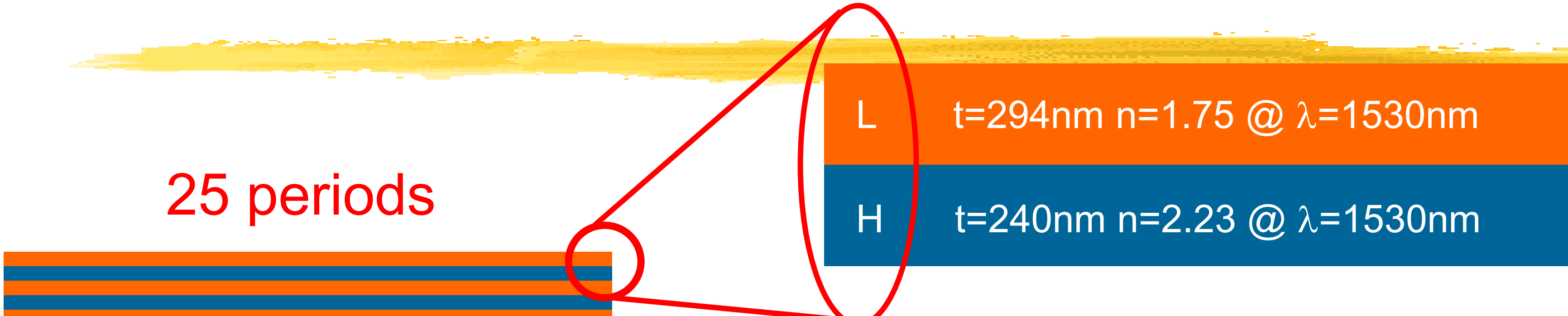


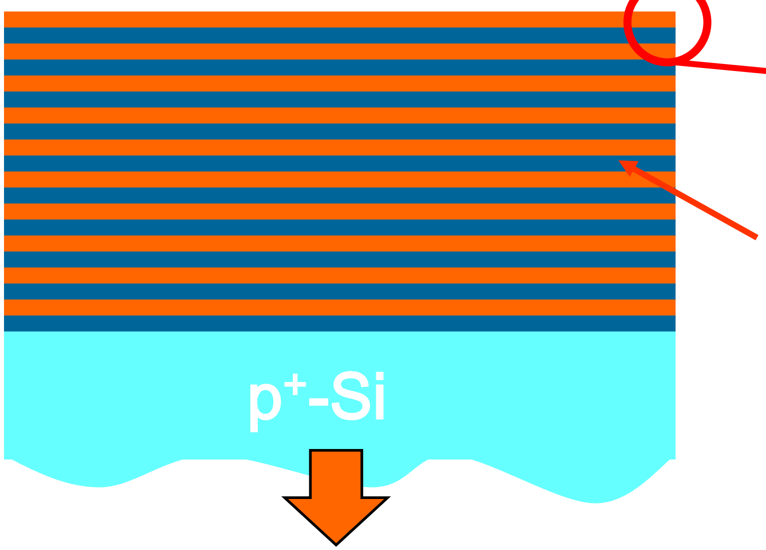
Free carriers absorption in p^+-Si makes that we cannot operate in the Kretschmann configuration

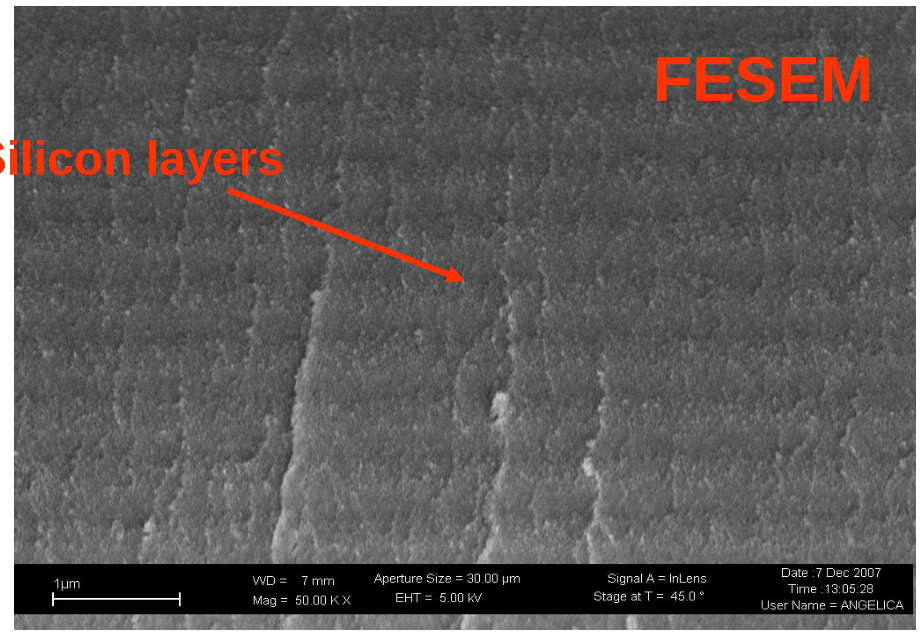


Otto coupling configuration

Porous Silicon Multilayer – 25 periods

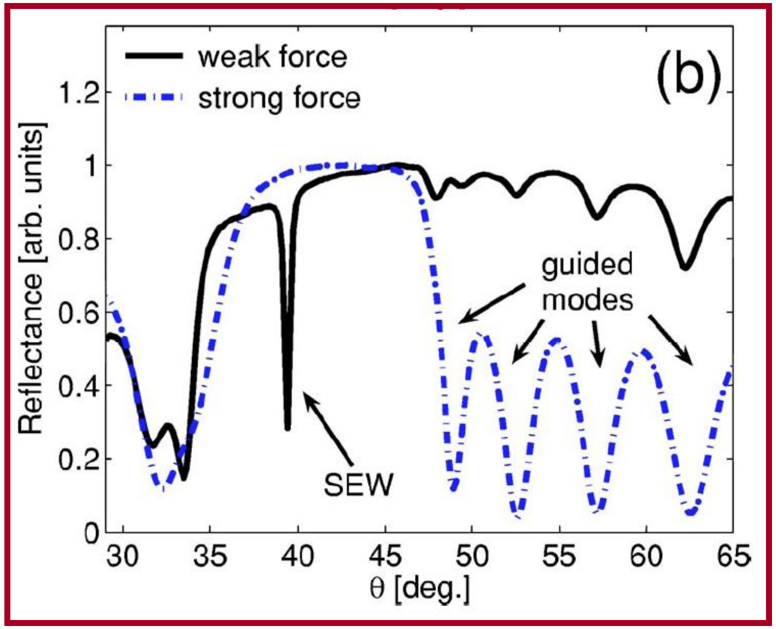




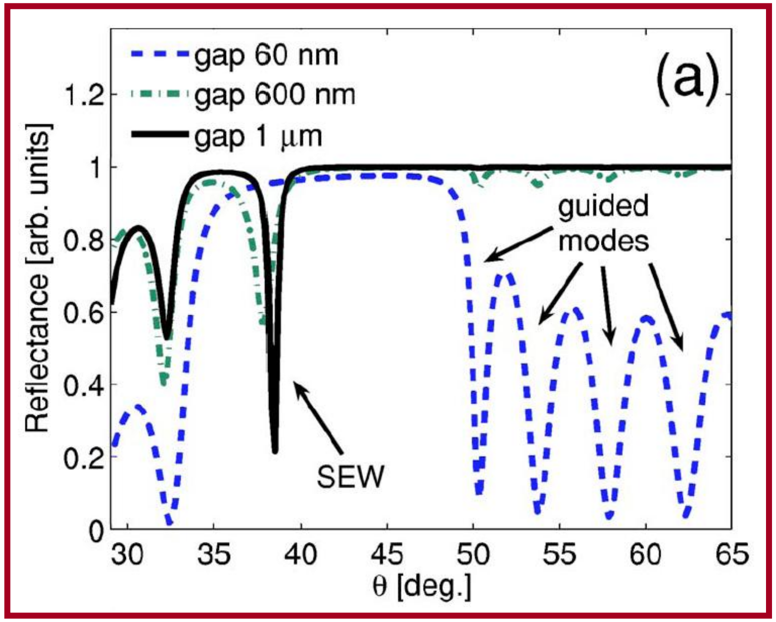


Free carriers absorption in p^+-Si makes that we cannot operate in the Kretschmann configuration

Porous Silicon Multilayer – 25 periods – Otto coupling conditions

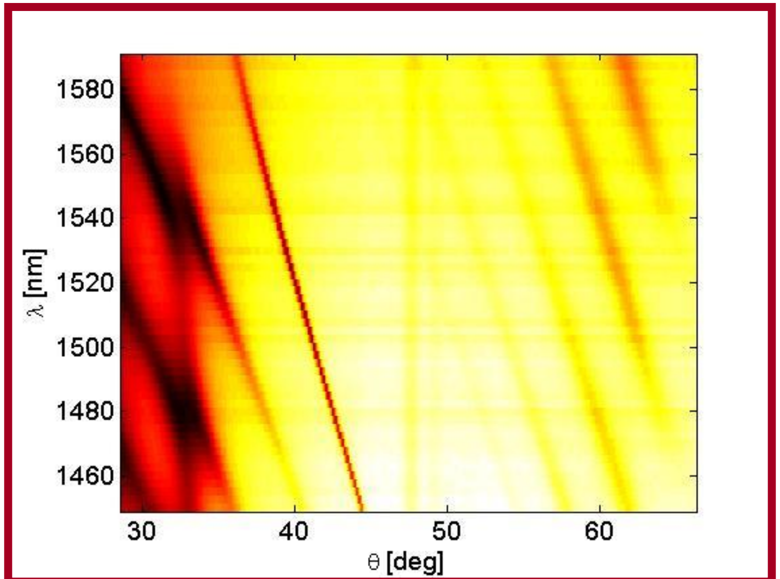


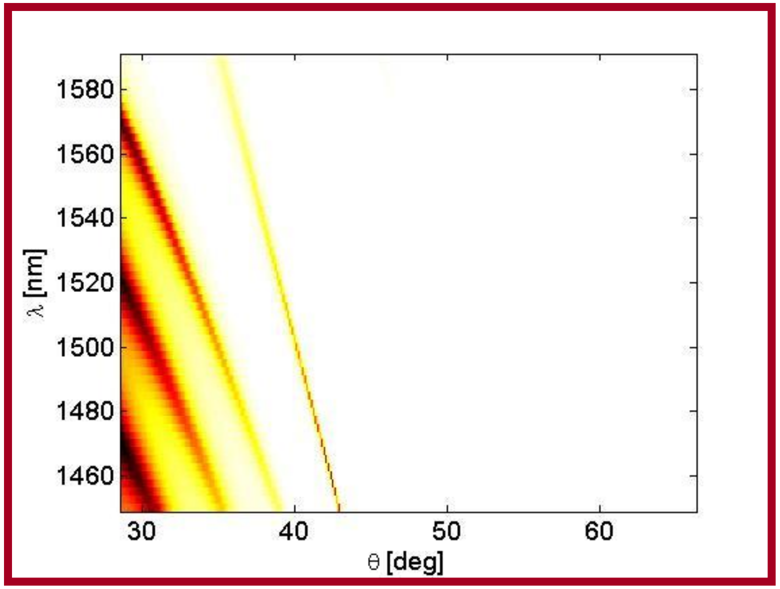
Measured



Theoretical

Porous Silicon Multilayer – 25 periods – SEW dispersion

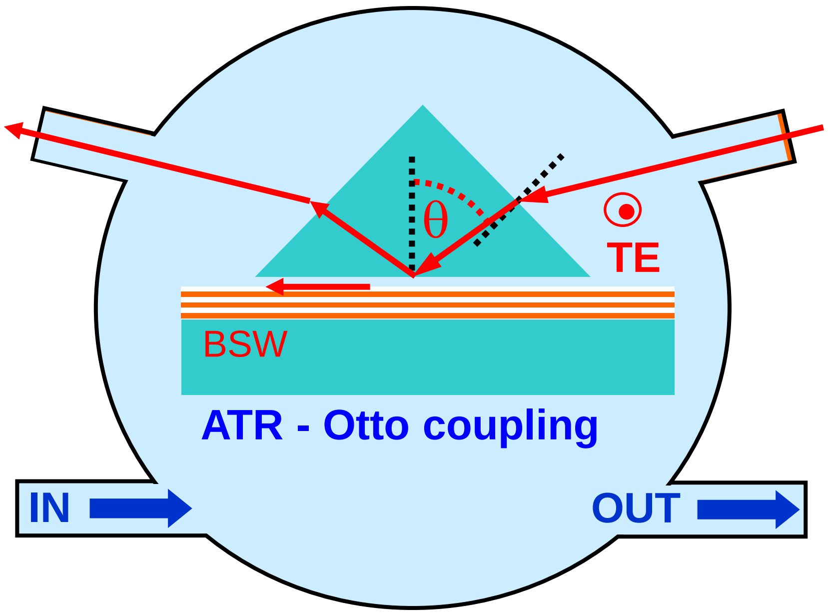




Measured

Theoretical

Porous Silicon Multilayer – 25 periods – Exposition to ethanol vapours



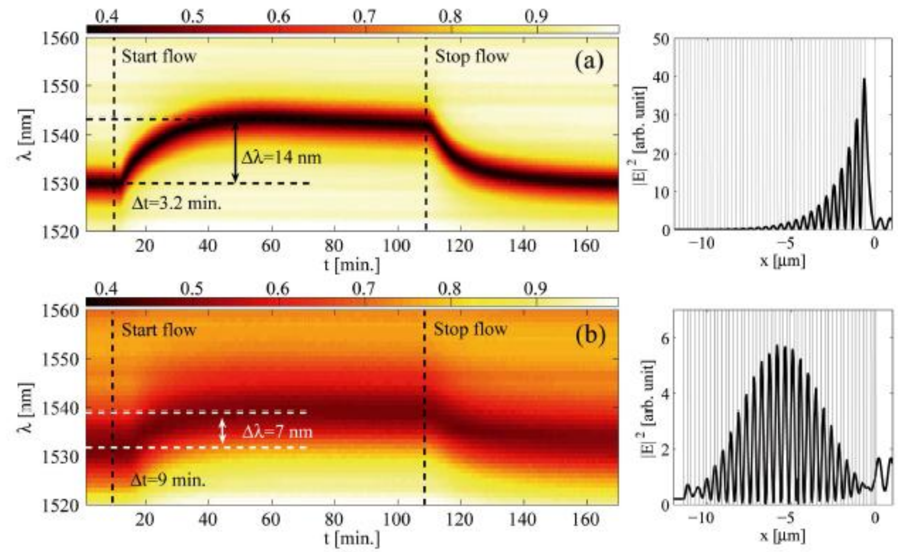
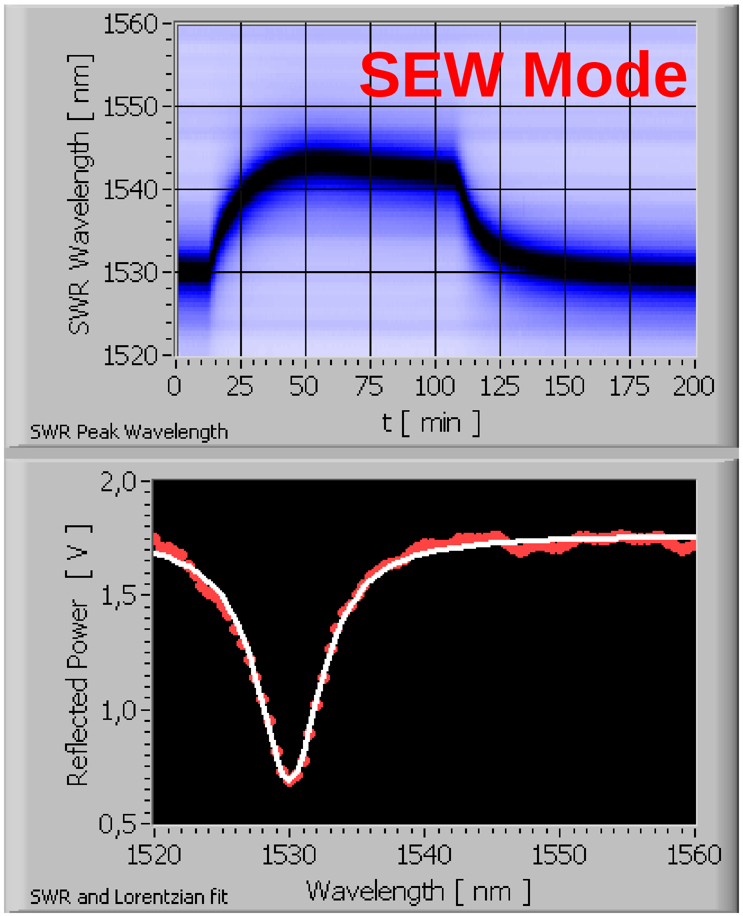
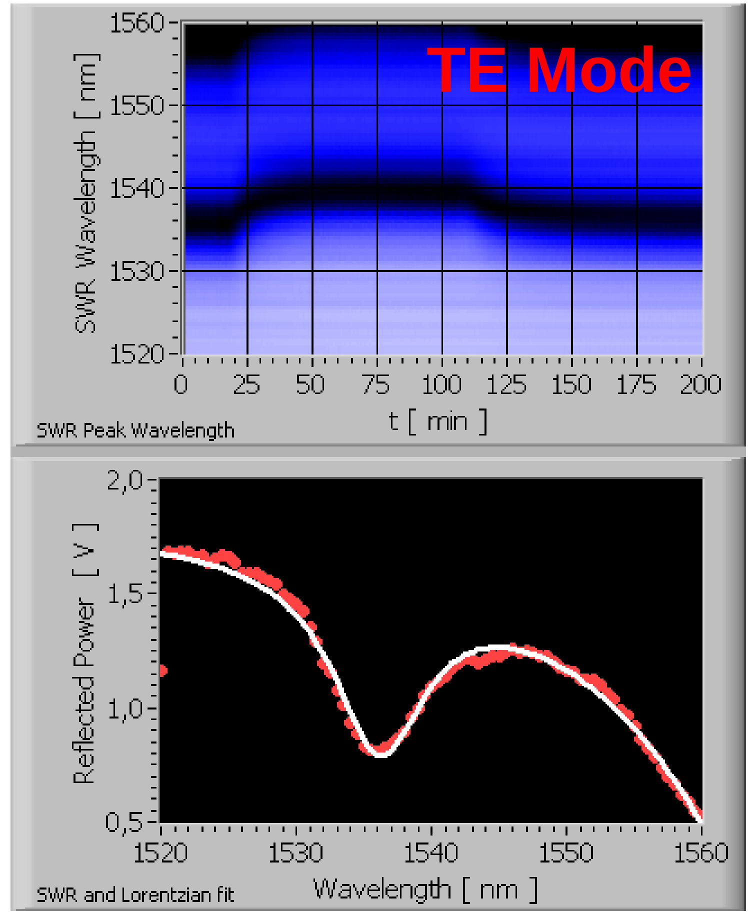


FIG. 4: Real-time measurement of the reflected light in the spectral range $\lambda \in [1520, 1560]$ nm from the p-Si multilayer exposed at ethanol vapor during a limited time interval. (a) SEW at $\theta = 37.60°$, (b) guided mode at $\theta = 47.49°$. Field intensity distributions of the selected modes are shown beside.

Appl.Phys.Lett. **91**, 241109 (2007)

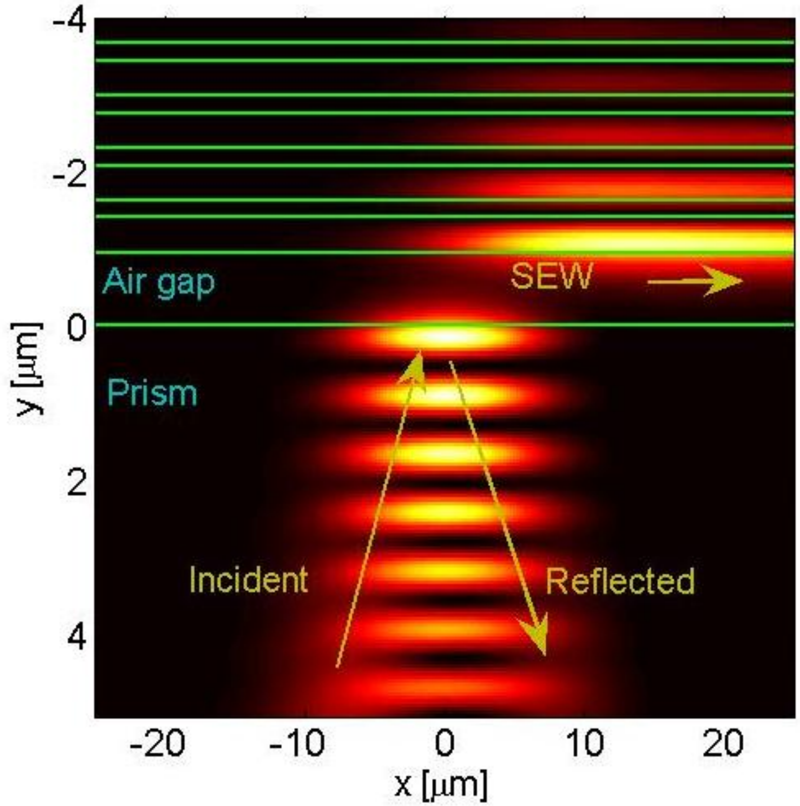
Porous Silicon Multilayer – Ethanol vapour sensing



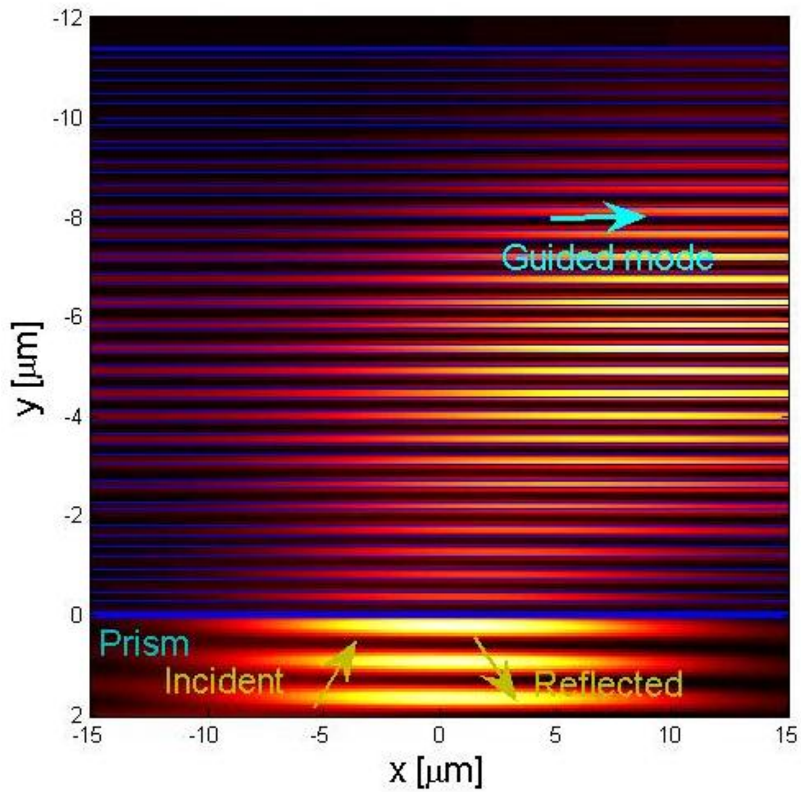


Porous Silicon Multilayer – Ethanol vapour sensing

BSW Coupling



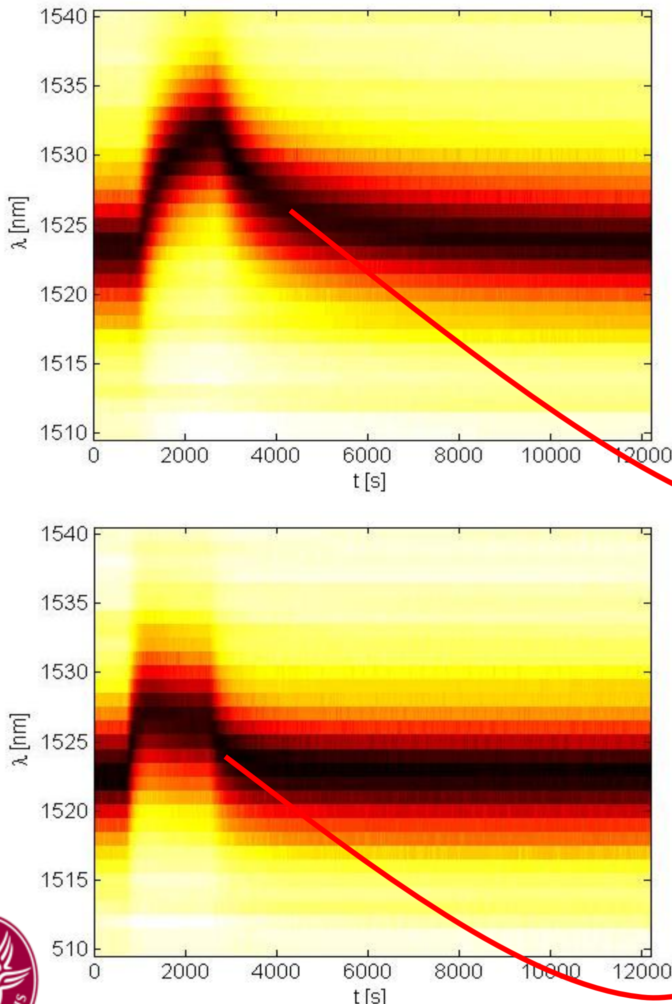
TE Mode Coupling

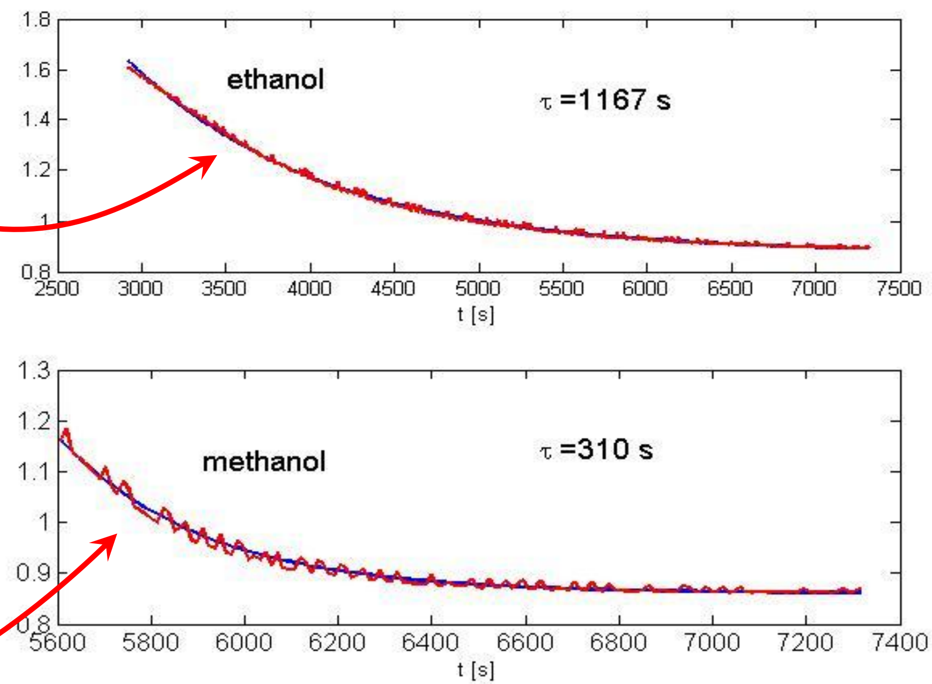


Porous Silicon Multilayer – 25 periods – Ethanol vs Methanol sensing

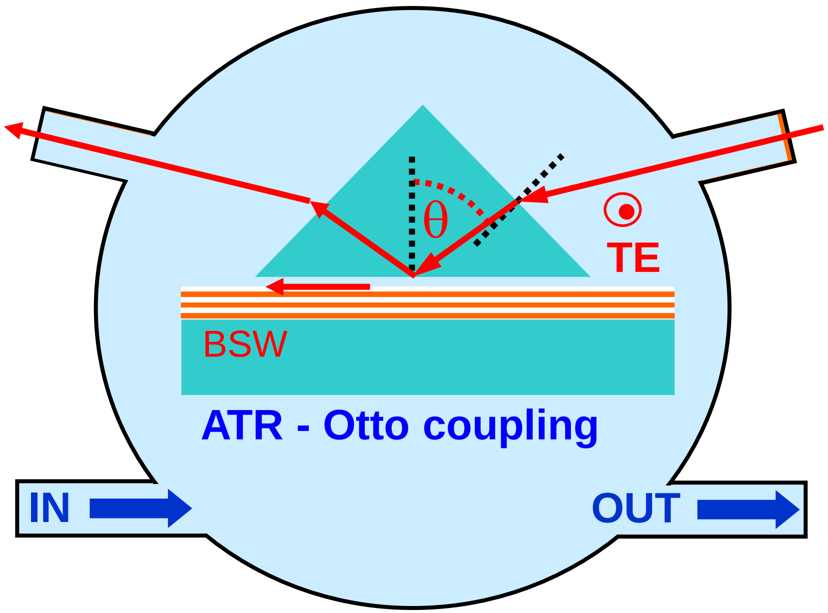
$$M_{ethanol} \cong 7.67 \cdot 10^{-26} kg \qquad n_{ethanol} = 1.36$$

$$M_{methanol} \cong 5.3 \cdot 10^{-26} kg \qquad n_{methanol} = 1.33$$





Porous Silicon Multilayer – 25 periods – Exposition to ethanol vapours



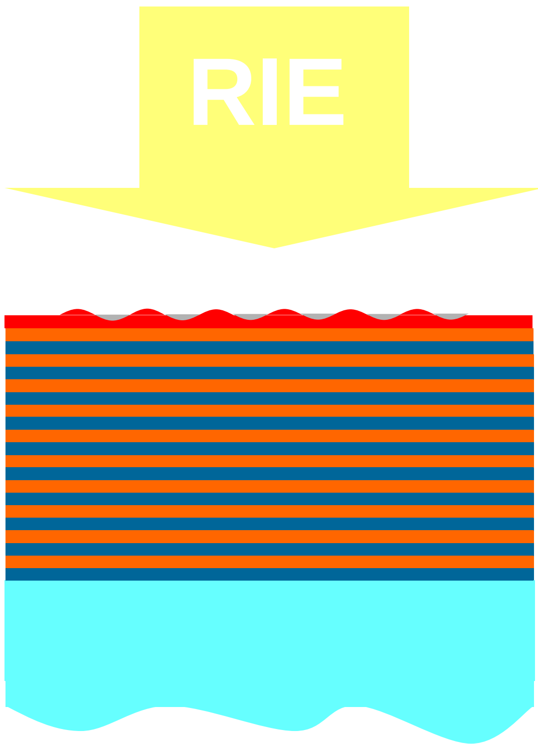
However the air gap is preventing the sensitive area to be exposed to the vapours and the response time of the sensors is extremely slow.

The sensitive surface

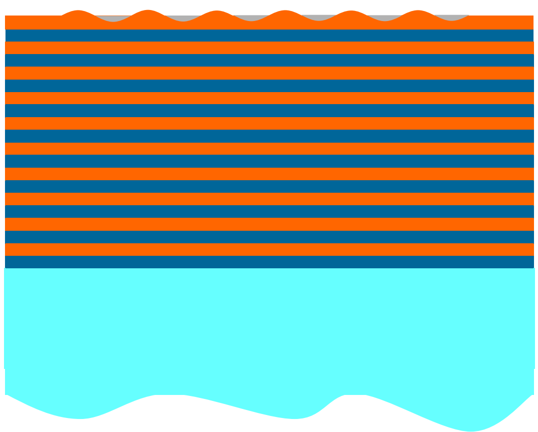
must be exposed

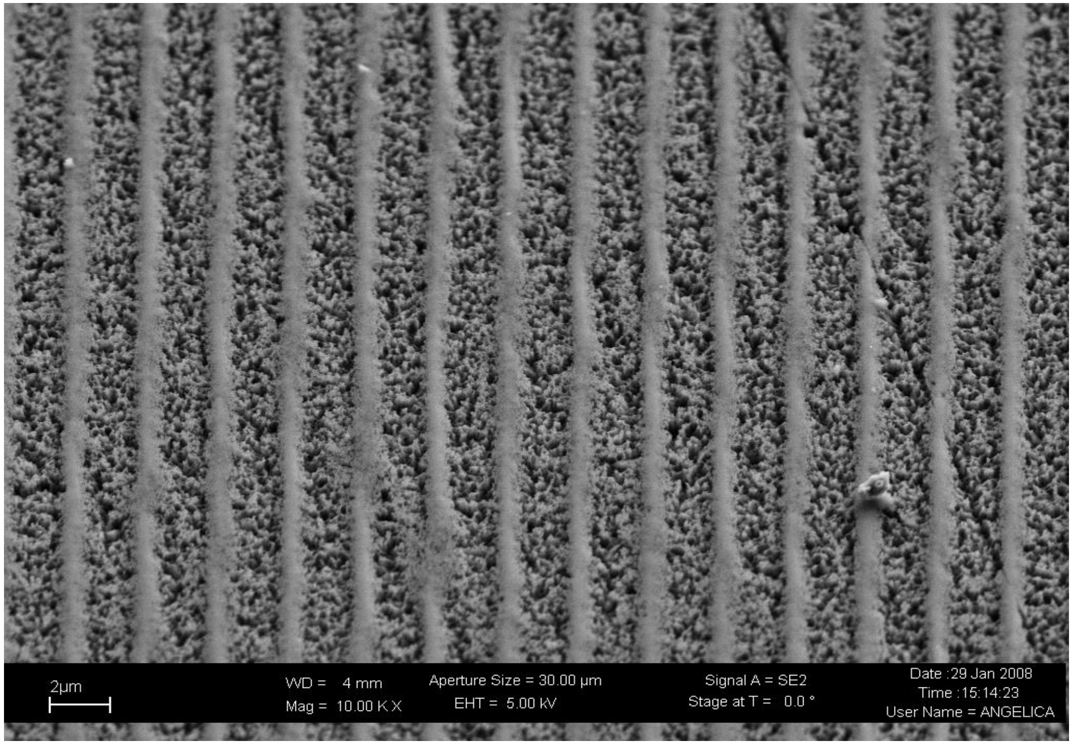
HOW?

SOLUTION 1 - Grating coupling



SOLUTION 1 - Grating coupling





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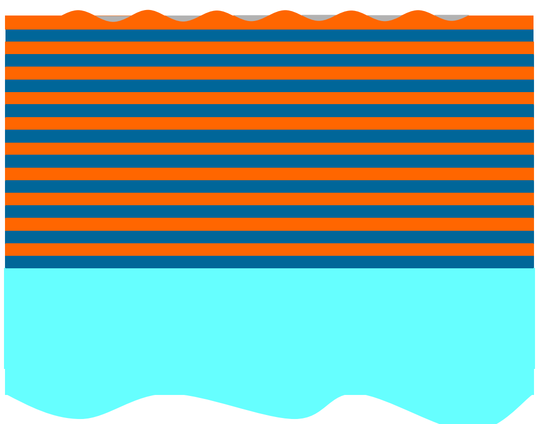

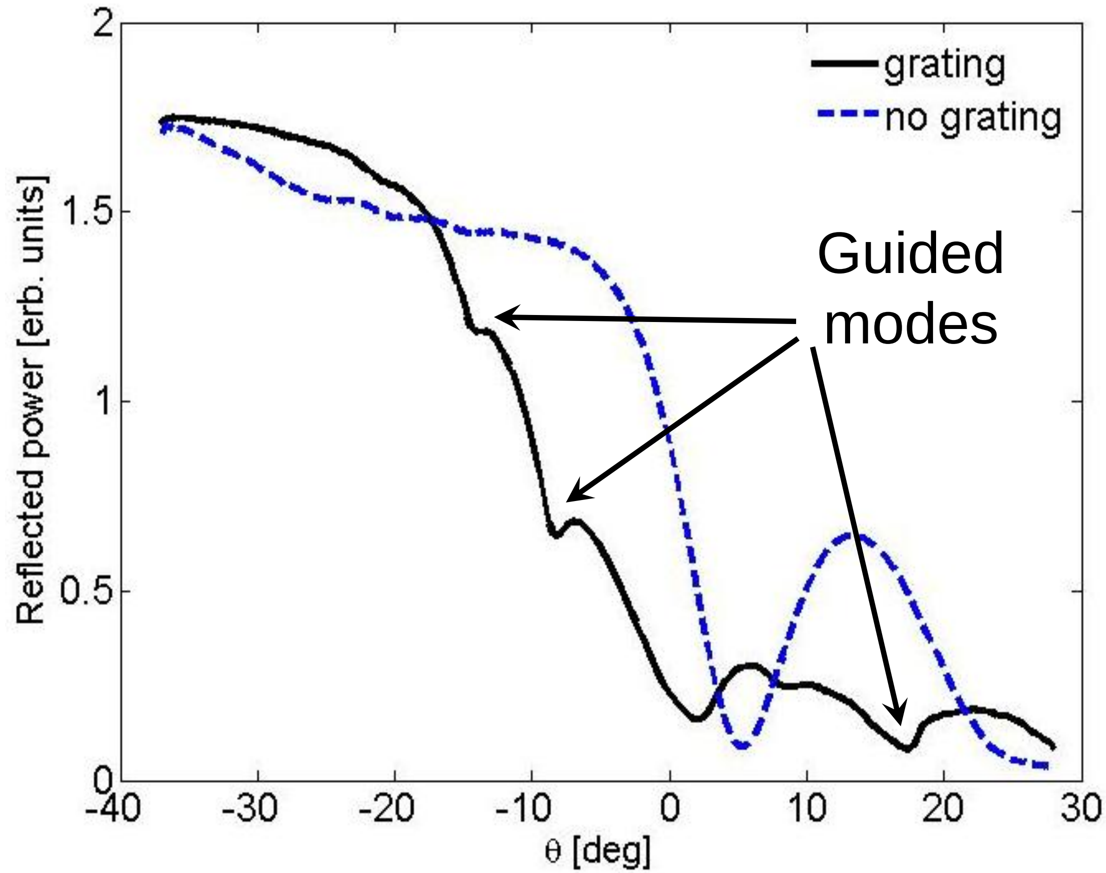

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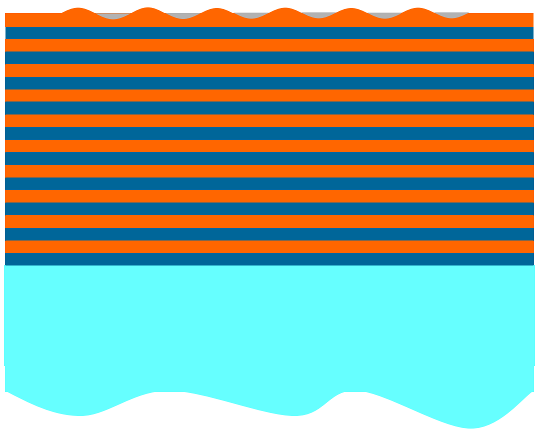

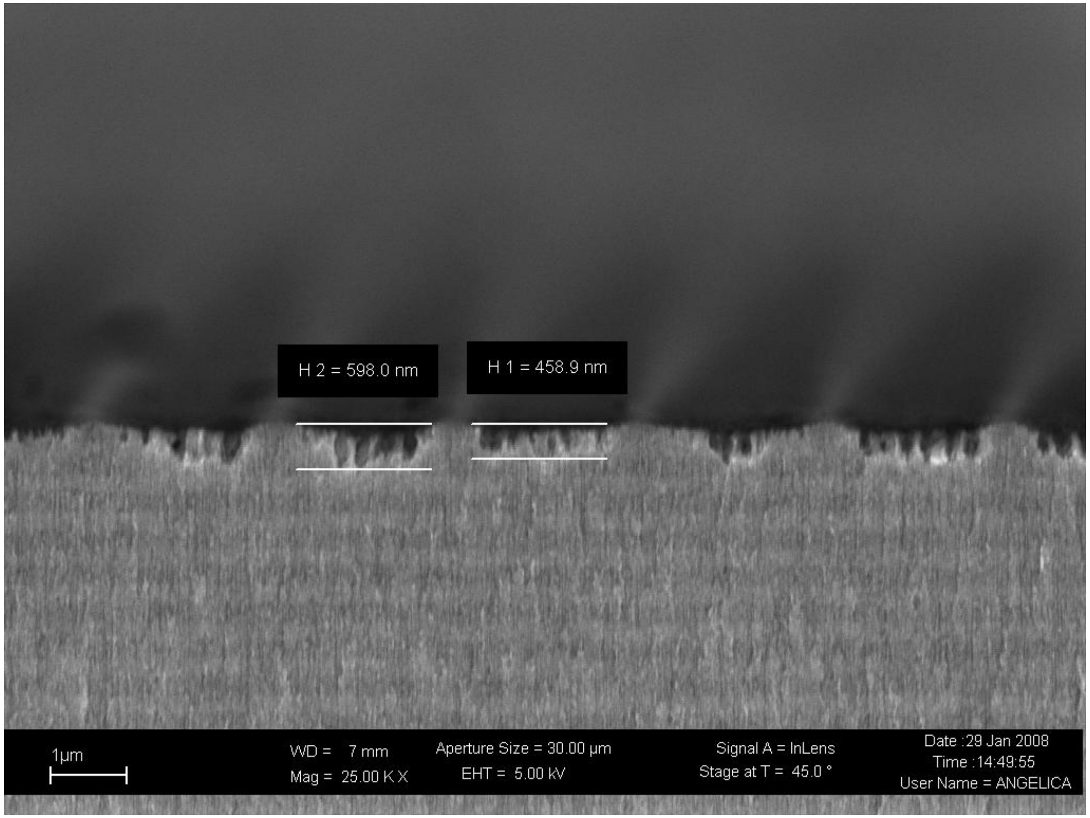

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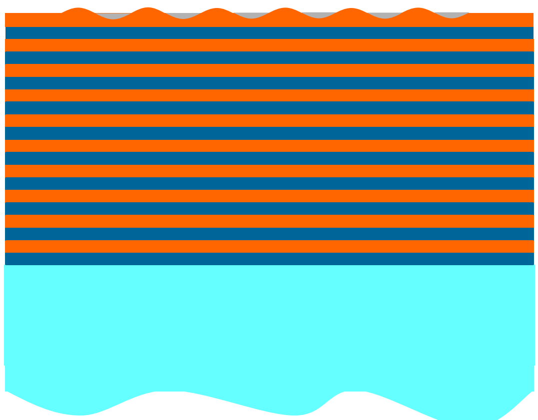
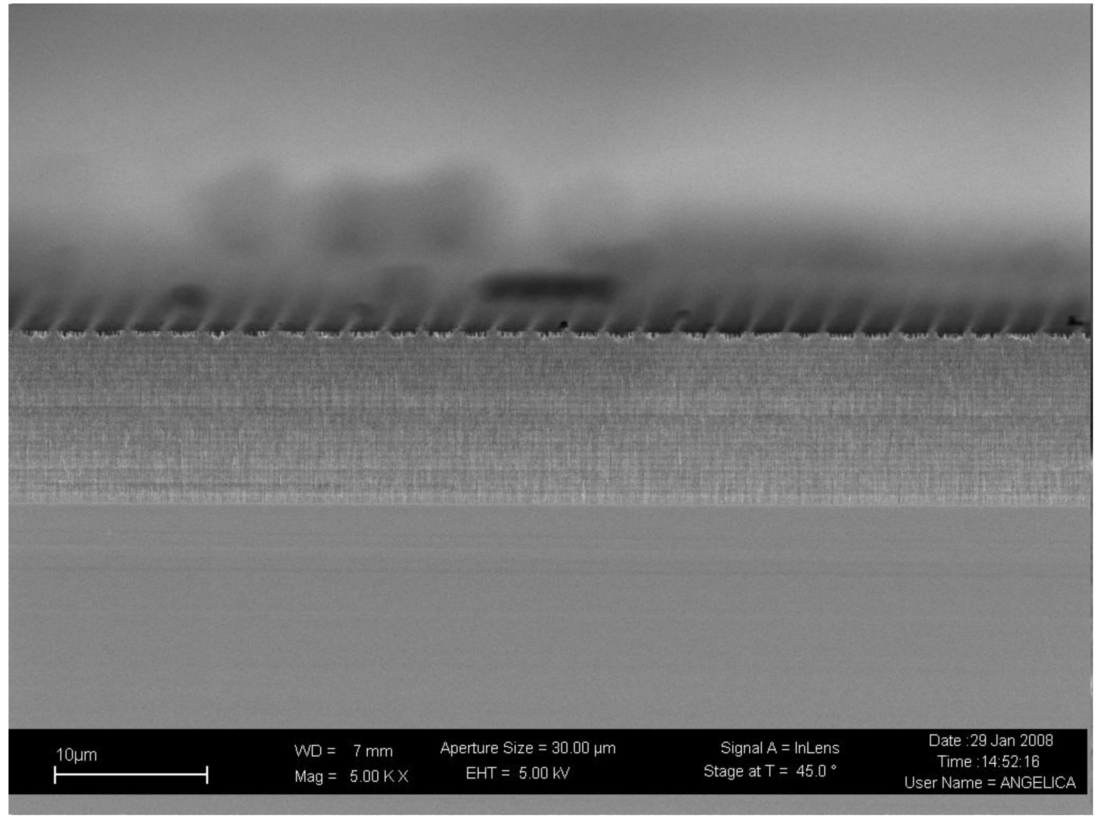
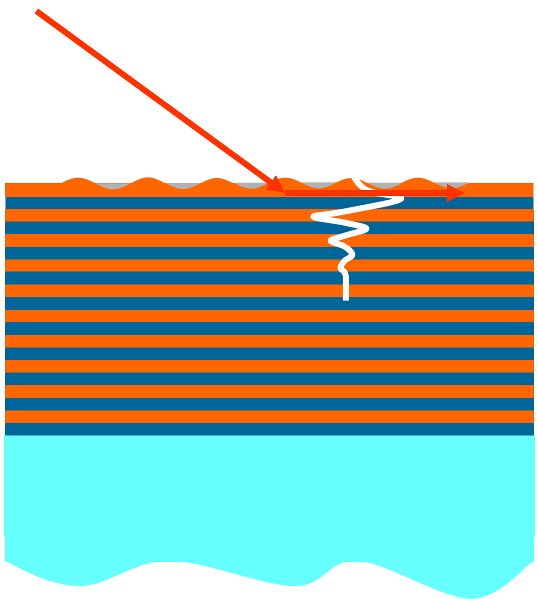
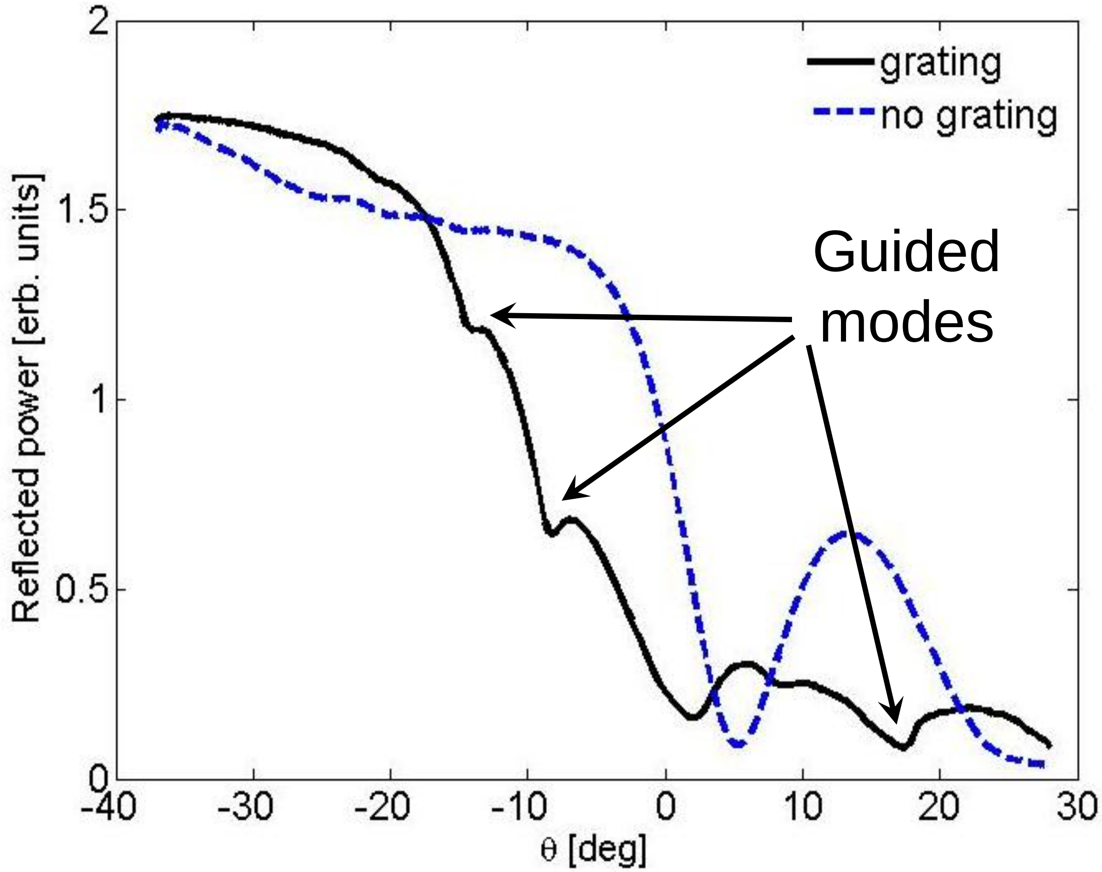




SOLUTION 1 - Grating coupling

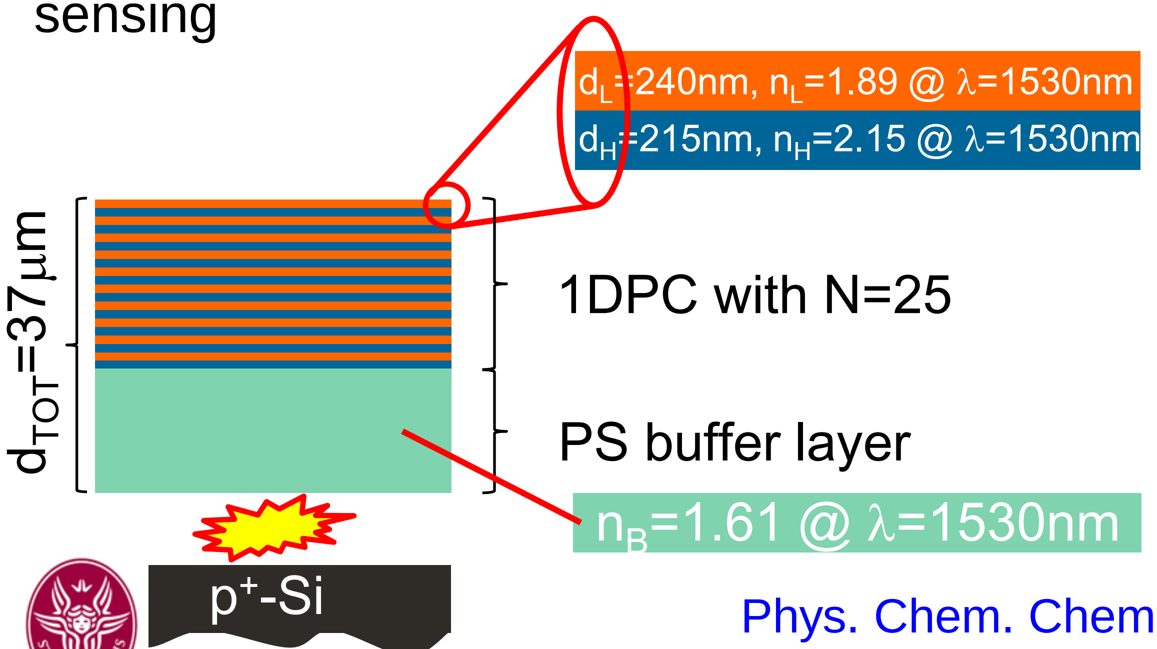


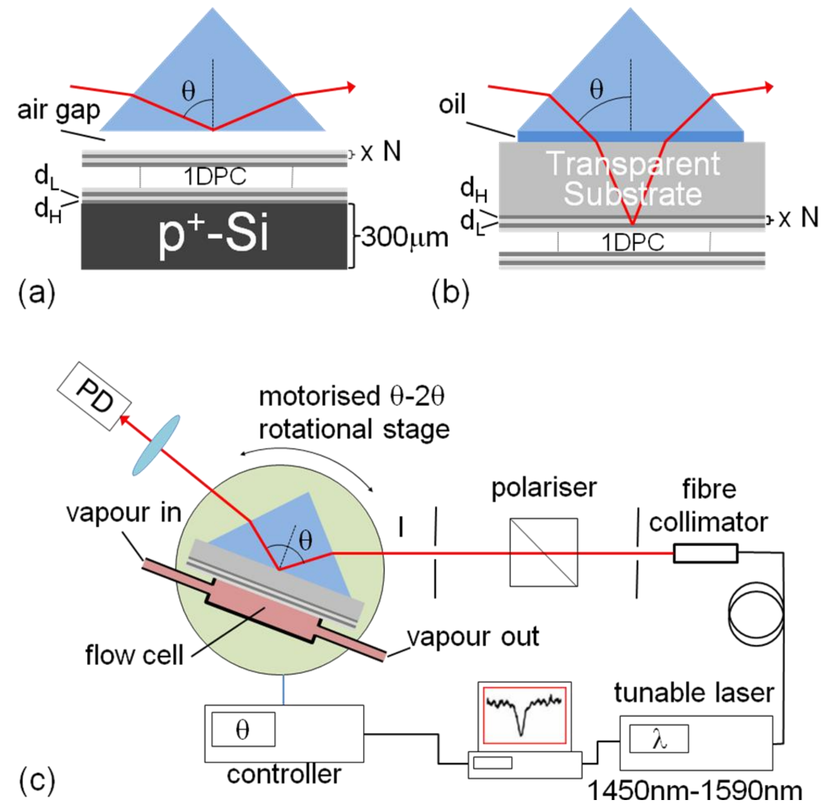


SOLUTION 2 - Free standing membranes - Real-Time Gas Sensing

SOLUTION 2

Detach a membrane by a high current intensity pulse and glue it on a glass substrate by a photoresist layer with the 1DPC surface free to be exposed for gas sensing

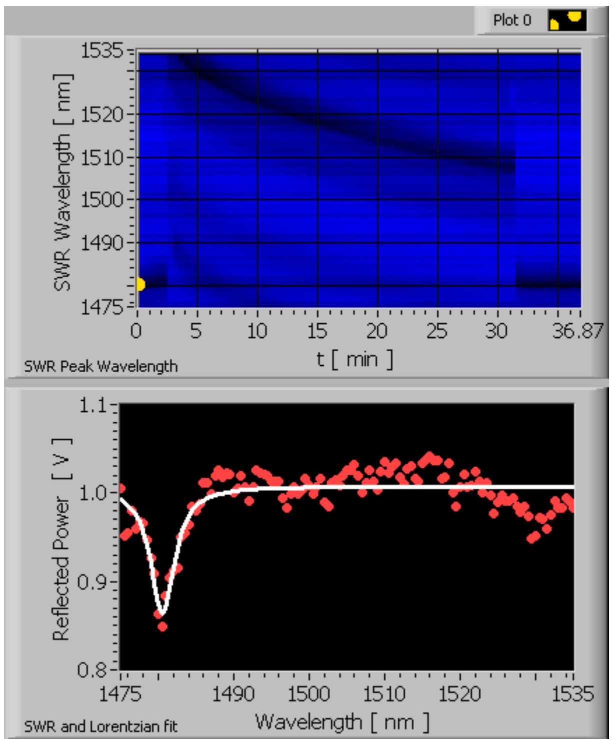




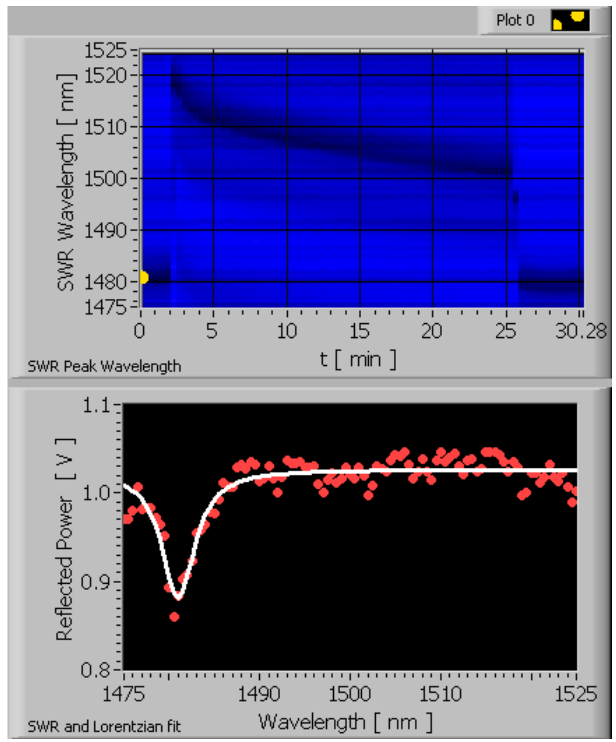
Phys. Chem. Chem. Phys., 12(2), 502 (2010)

Patent Pending, PCT Procedure

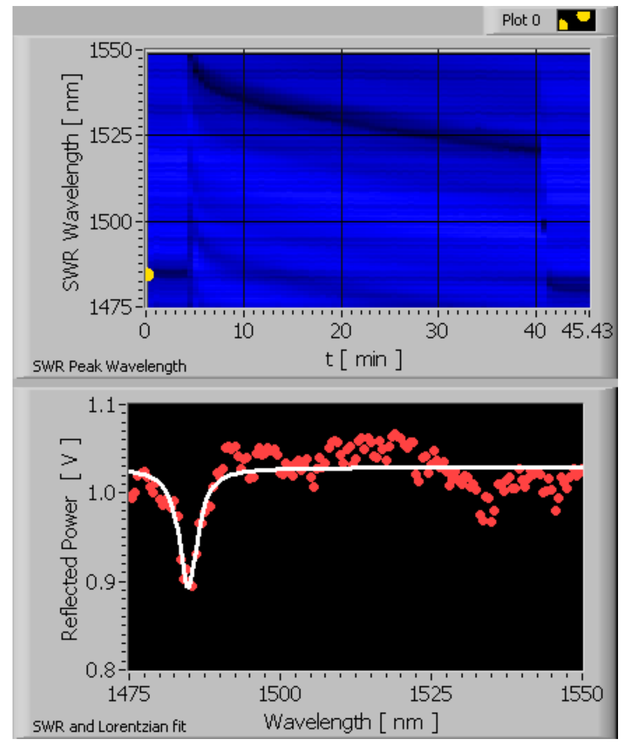
SOLUTION 2 - Free standing membranes - Real-Time Gas Sensing



Methanol

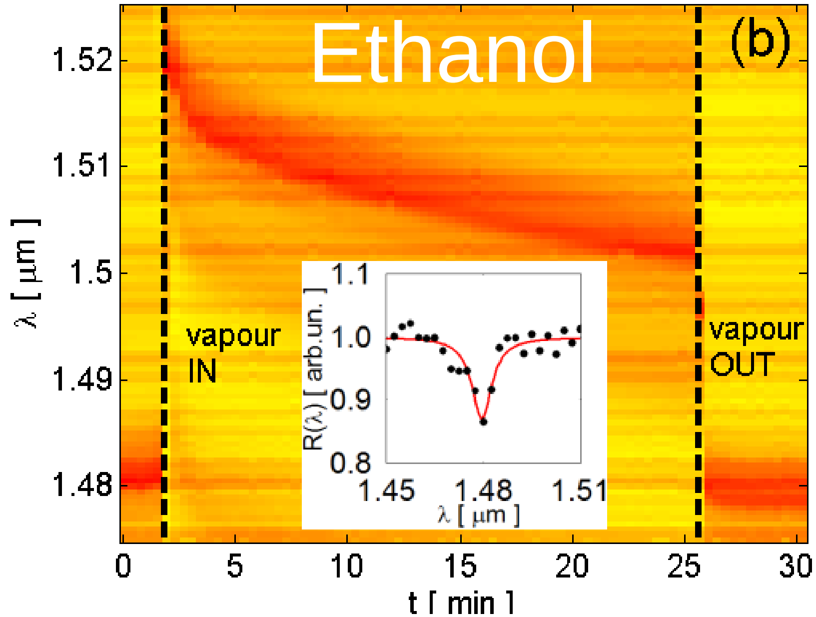


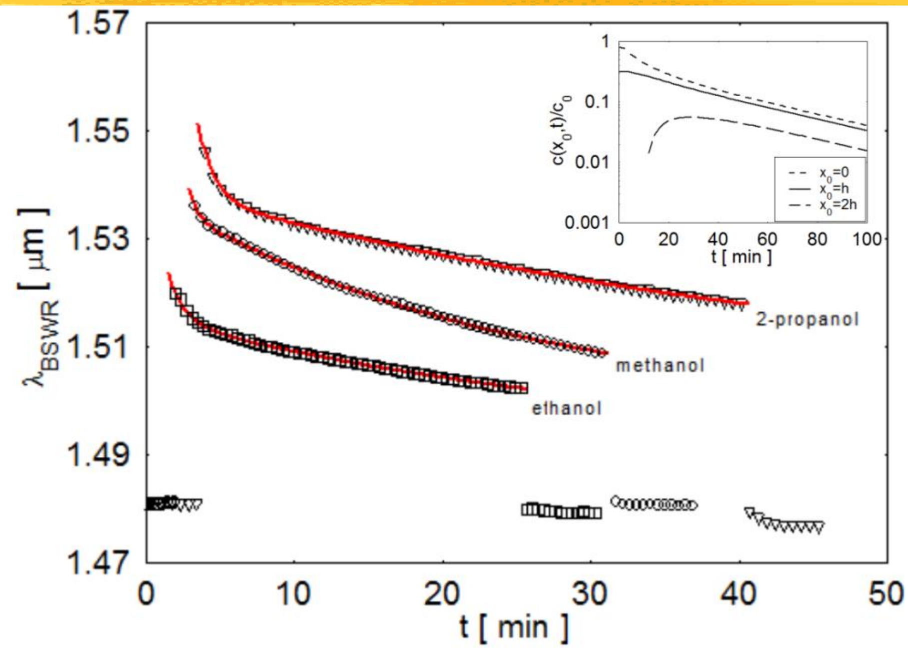
Ethanol



2-Propanol

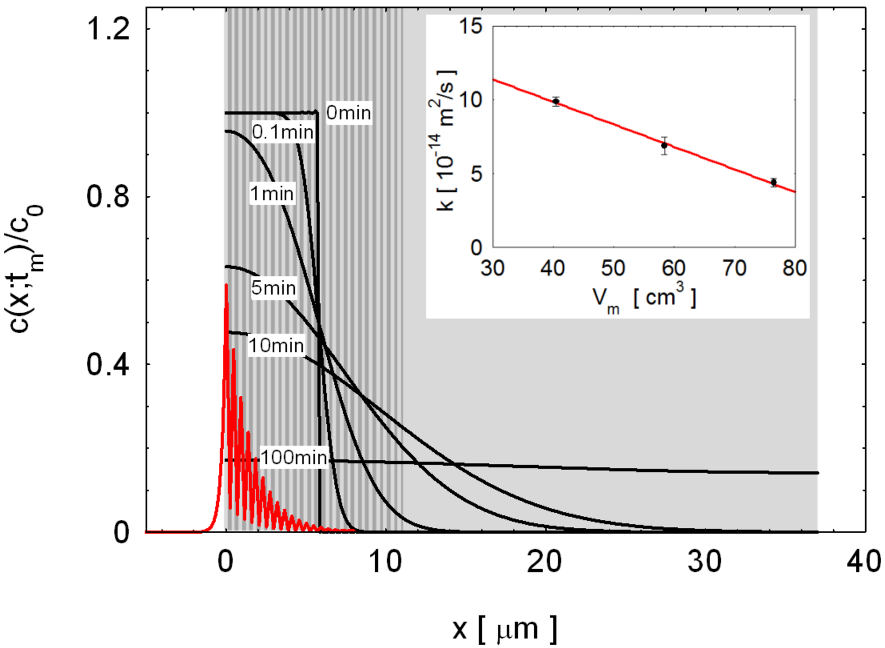
SOLUTION 2 - Free standing membranes - Real-Time Gas Sensing





Vapour	p_0[a] [kPa]	m_V [μg]	p [g/cm^3]	n	$\Delta\lambda_{MAX,EXP}$ [nm]	τ_S [min]	τ_L [min]	k [10^{-14}m^2/s]
Methanol	16.20	293	0.792	1.33	56.3	0.6±0.1	24.4±0.8	9.9±0.3
Ethanol	7.54	196	0.789	1.36	39.8	1.14±0.07	33±3	6.9±0.6
2-Propanol	5.87	199	0.786	1.38	66.4	1.09±0.05	52±3	4.4±0.3

Application to Real-Time Gas Sensing



Diffusion equation

$$\frac{\partial^2 c(x,t)}{\partial x^2} = \frac{1}{k}\frac{\partial c(x,t)}{\partial t}$$

Initial conditions

$c(x,0) = c_0$ for $0 \le x \le h_0$

$c(x,0) = 0$ for $h_0 < x \le L$

Boundary conditions

$\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=0} = 0$ for $t > 0$

$\left.\frac{\partial c(x,t)}{\partial x}\right|_{x=L} = 0$ for $t > 0$

Solution

$$c(x,t) = c_0 \cdot \left[\frac{h_0}{L} + \frac{2}{\pi}\sum_{\alpha=1}^{\infty}\frac{1}{i}\sin\left(\frac{\alpha\pi h_0}{L}\right)e^{-k\left(\frac{\alpha\pi}{L}\right)^2 t}\cos\left(\frac{\alpha\pi}{L}x\right)\right]$$

Equating the measured time constants t_L to $k(\pi/L)^2$ we extracted the diffusion coefficients k for the three alcools in the PS structure that scale linearly with respect to the molecular volume.