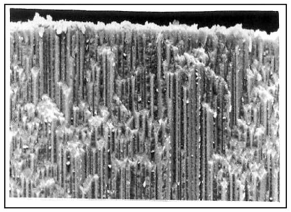
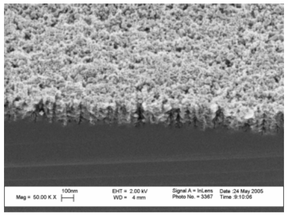
A brief overview of porous silicon


Micrograph of electro-etched porous silicon surface (from Sailor)



Part I

Felix Lu

Duke University

Sept. 29, 2006


James Gole displays a treated silicon wafer illuminated by ultraviolet (purple) light. The orange-red photoluminescence from the porour silicon is clearly visible.

Pictures from http://www.ghuth.com/vision/?p=7, http://bios.ewi.utwente.nl/research/micronanofluidics/solvingmicromachining.doc/index.html and http://gtresearchnews.gatech.edu/newsrelease/SISENSOR.htm

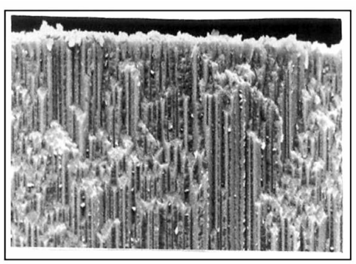
Outline

- What is porous silicon?
- Why is it interesting?
- How is it made?
- Features and controllability
- Applications
- Summary

What is porous silicon?

- Electrochemically etched silicon
  - Pores : nm → µm sized
  - Pore nucleation – many models [1,2] Suggests defects near surface play primary role
- Discovered in 1956 by Arthur Uhlir at Bell Labs, doing some electro-polishing experiments

Type of porous Si	Corresponding size regime for dominant porosity (nm)
Microporous	<= 2
Mesoporous	2-50
macroporous	> 50



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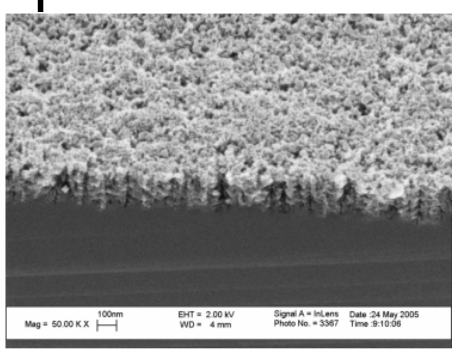


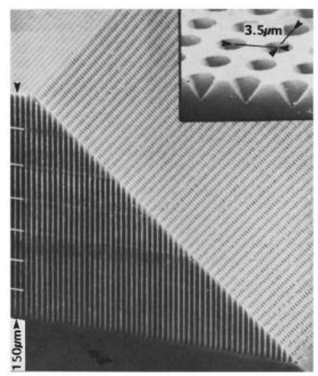


FIG. 9. Plan-view, cross-section and 45° bevel of a aligned macropore formed from lithographically-defined initial pits (inset) in n^- Si (from 66).

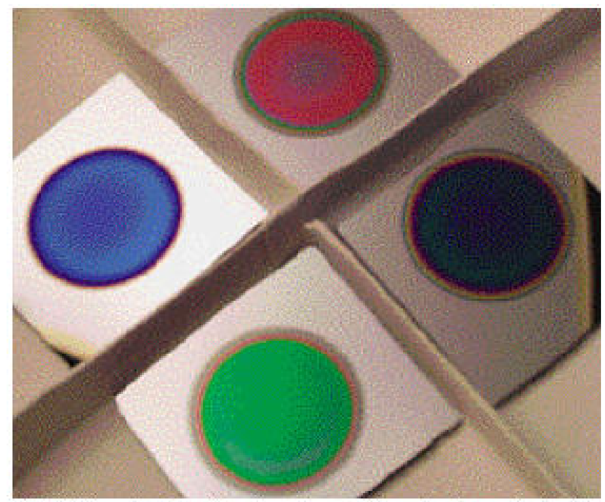


Fig. 3 This image shows four different types of porous silicon, where the pore size is varied. Thus, since pore size determines the luminescence spectrum the chips are different colors. (Courtesy Rochester University.)

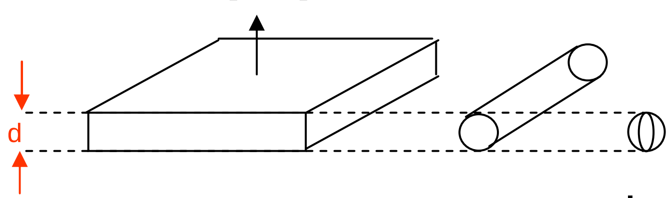
George Marsh, Materials Today January 2001

Why is it interesting?

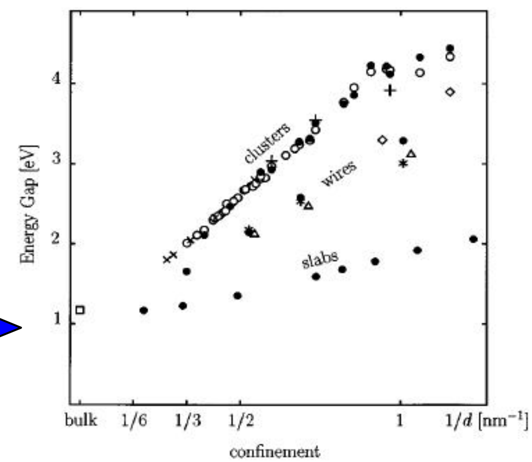
- CMOS compatibility
  – light emission in silicon!

Color	Peak wavelength (nm)
UV	~350
Blue-green	~470
Blue-red	400-1100
Near IR	1100-1500

  – Large surface area to volume ratio
    - Surface area ~200-1000 m^2/cm^3 [4,7]
  – nanometer size effects
    - Increases bandgap [2,3]



As ‘d’ decreases, E_g increases



B. Delley and E. F. Steigmeier, **Size dependence of band gaps in silicon nanostructures,** Appl. Phys. Lett. **67** (16), 16 October 1995, p. 2370

* For fun & comparison, 1g activated carbon ~ 400-1500 m^2 surface area

Why is it interesting? (cont’d)

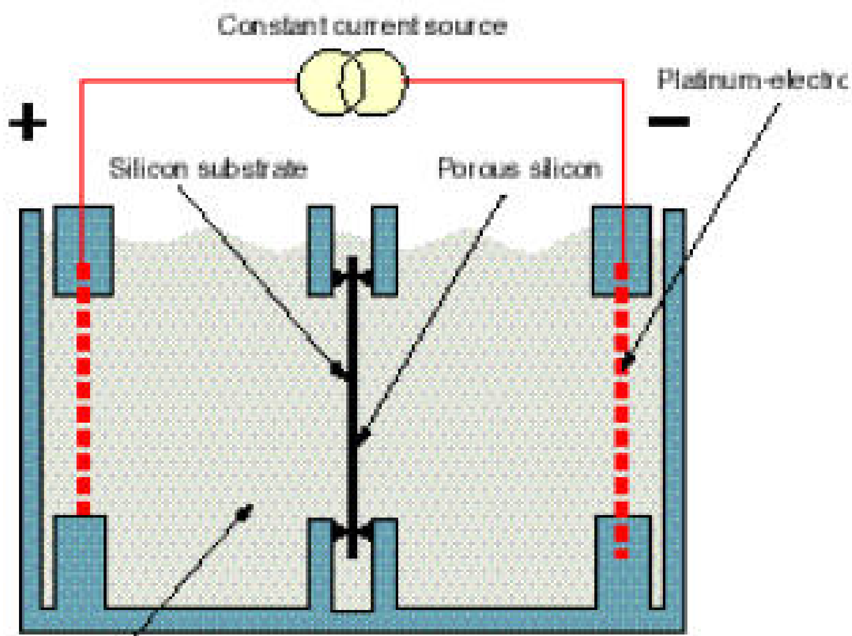
- Optoelectronic properties a function of skeleton size
- Feature sizes are dynamically controllable
- Seems to be biologically compatible
  - The range of tunable pore sizes (2 to 2000 nm) in porous silicon, size of a small DNA fragment ~10-30 nm nanometers, proteins ~100-nm, and bacteria and cells ~several microns diameter.
  - slow release of drugs
  - sensitive biosensor for proteins, antigens, and DNA, and it can be modified with a wide range of biological or organic molecules. (http://oemagazine.com/fromTheMagazine/mar03/silicon.html)
- Cheap to fabricate

Other Porous semiconductors

- SiC – blue or UV emission
- GaP, $Si_{1-x}Ge_x$, Ge, GaAs, InP

} Not enough data to establish if PL due to size effects

How is porous silicon made?



George Marsh, Materials today January 2001

Similar to a CP4* etch (HF/HNO_3) where the nitric acid (strong oxidizer) injects holes into the Si to dissolute the surface.

Aqueous solution of HF-ethanol [4]

Ethanol acts as a surfactant to penetrate pores and to minimize hydrogen bubble formation [5]

Electrochemical etch

Si wafer = anode, Pt = cathode
(Pt used because it is resistant to HF)
Dissolution of Si occurs only under anodic polarization. [4, pg 9]

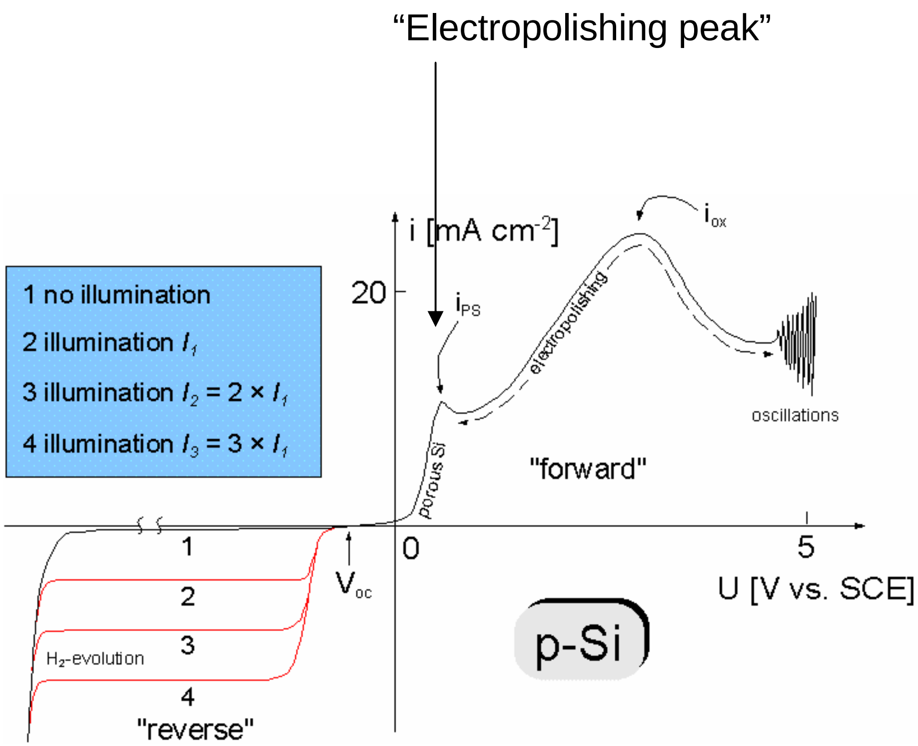
Anodic polarization =

forward biased if Si is p-type

reverse biased if Si is n-type

* Stands for concentrated piss, http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_4/advanced/t4_2_2.html

How is porous silicon made?



http://www.tf.uni-kiel.de/matwis/amat/poren/eccv.html

Main requirements for PS formation[4]:

1. The Si wafer must be anodically biased.

2. For n-type doped and semi-insulating p-type doped Si, light must be supplied.

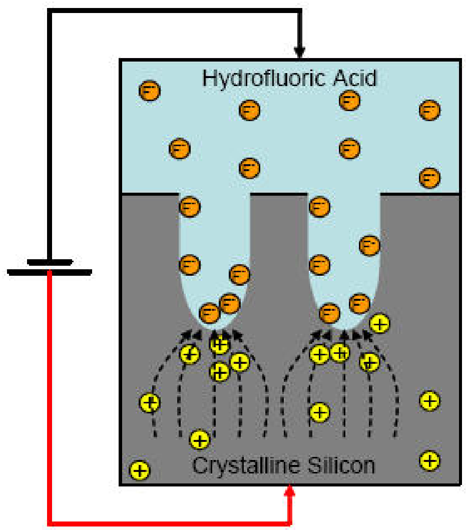
3. Current densities below the critical value, j_{PS}, must be used.

Etching requires holes (electron injection) to break bonds. The PS left is depleted of holes.

Resistivity ~ 10^6 Ω·cm similar to intrinsic Si [4(page 9), 8]

SCE = standard calomel electrode = reference electrode - for more details, see http://chem.ch.huji.ac.il/~eugeniik/refelectrodes.htm

PS fabrication controllability



http://www.ece.rochester.edu/~ouyang/papers/OpticsEast_ouyang.pdf

Inject current (holes) into Si

- the etching path and rate can be controlled
- holes congregate at the tips of the etch pores.

This allows modulation of the porosity in the sample.

- **Topics that are not well understood in the literature include**: [6]
  - Orientation dependence
  - Effect of doping level
  - Effect of ε, conductivity and temperature of electroyte

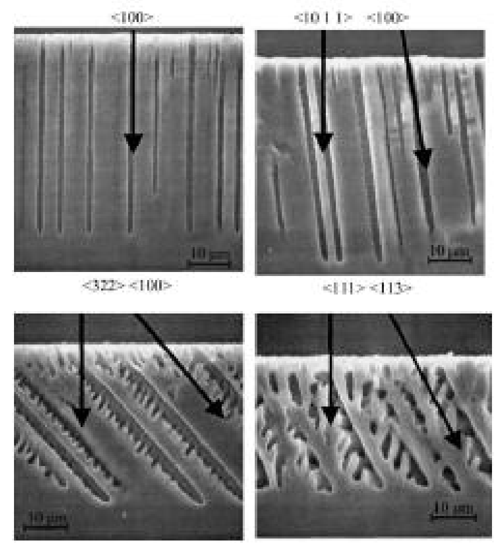


Fig. 5. Orientation dependence of (random) n-macropores(aqu/bsi). The substrate orientation is (a) (1 0 0), (b) (10, 1, 1), (c) (3 2 2), and (d) (1 1 1). In (d) (1 1 3) oriented pore tripods result.

Foll et al. (2002) [Ref 6]

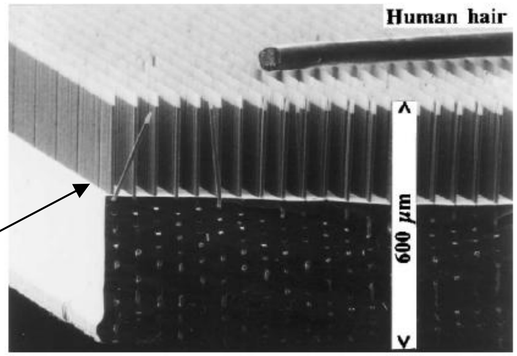
Features and controllability

- Pore size / wire size
  - Electrolyte type, HF concentration, doping type and level, illumination [6]
- Luminescence wavelength(s)
  - Stronger photo-luminescence with increasing porosity
- Absorption spectrum – distribution of porosity
- Aging properties – minutes to weeks
  - There is current work on stabilizing the surface reactivity

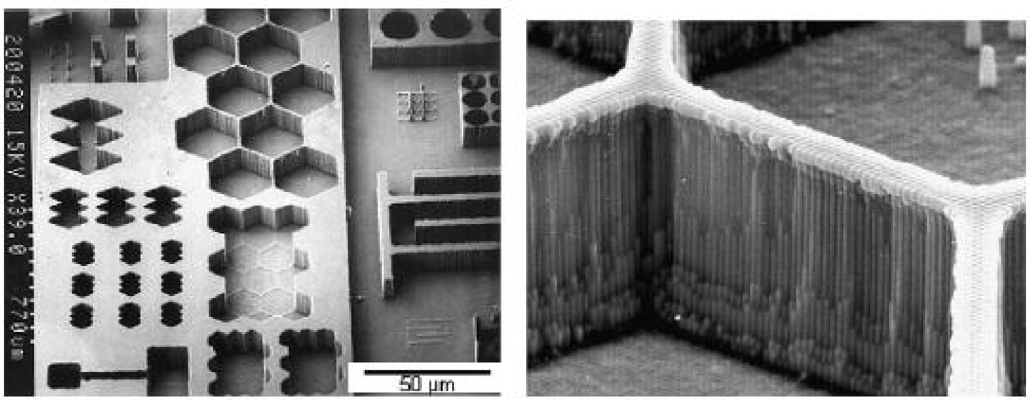
Applications

- MEMs

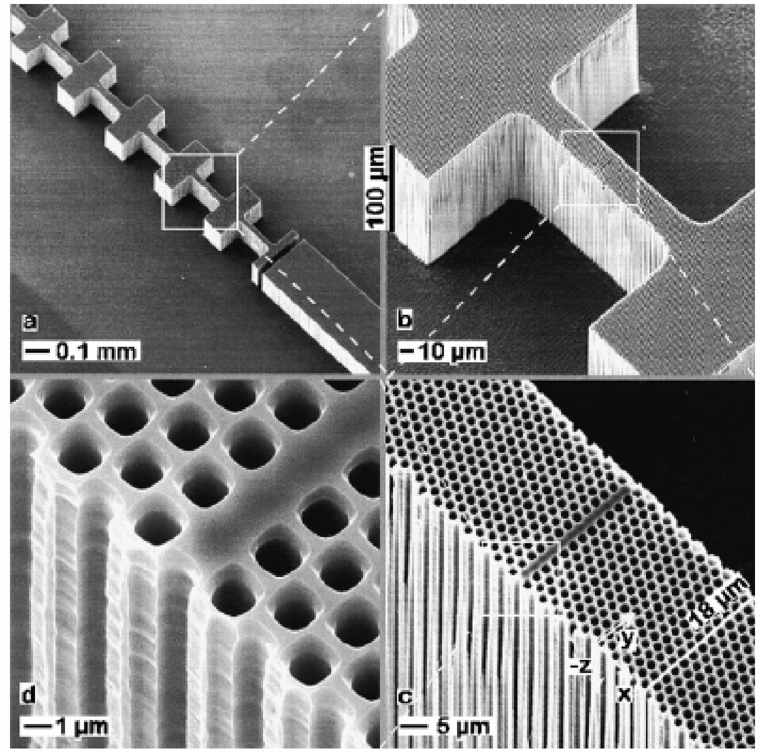
X-ray filter to block inelastically scattered photons



V. Lehmann, S. Ro¨nnebeck, Sens. Actuators A 95 (2001) 202.



From S. Ottow, V. Lehmann, H. Fo¨ ll, J. Electrochem. Soc. 143 (1996) 385, and S. Ottow, V. Lehmann, H. Fo¨ ll, Appl. Phys. A 63 (1996) 153.



Photonic crystal, from S.R. Nicewarner-Pena, R.G. Freeman, B.D. Reiss, L. He, D.J. Pena, I.D. Walton, R. Cromer, C.D. Keating, M.J. Natan, Science 294 (2001) 137.

Applications

- Bragg reflectors, AR coating, Waveguides from refractive index change (function of pore size)

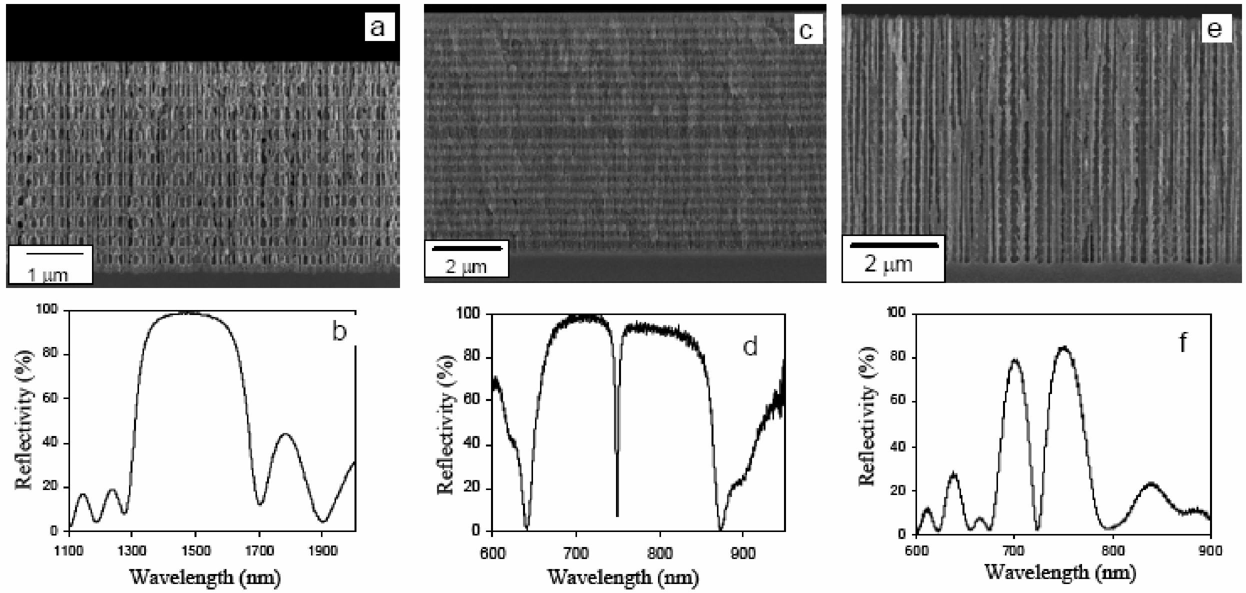


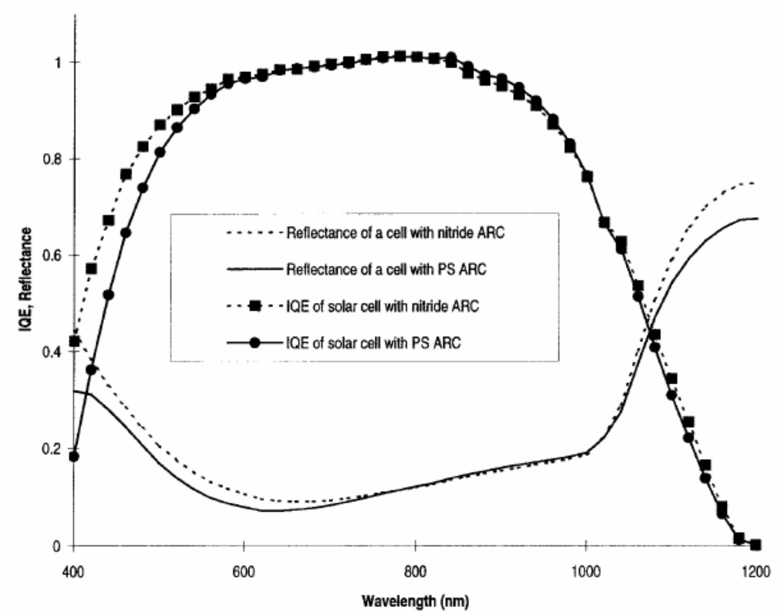
Fig. 5. (a) Cross sectional SEM image of a PSi Bragg mirror. (b) Reflectance spectrum of the Bragg mirror. (c) & (d) Cross sectional SEM image and reflectance spectrum of a mesoporous microcavity with layers of 75% and 50% porosity. (e) & (f) Cross sectional SEM image and reflectance spectrum of a macroporous silicon microcavity with layers of 80% and 75% porosity.

Huimin Ouyang and Phillipe Fauchet, SPIE Optics EAST 2005

Applications

- Solar cells
  (with PS AR coating)
  - large surface area and texturing for trapping light
  - behaves as a direct gap semiconductor**
  - broad spectrum of E_g's (from broad PL band)
    - make it favorable for harvesting a larger amount of the solar spectrum.

Monocrystalline silicon solar cell with PS AR coating

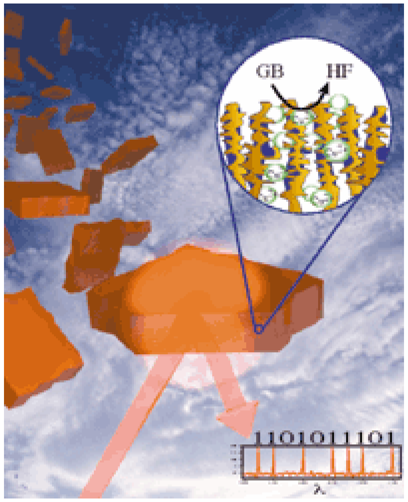


Renet R. Bilyalov, et al., IEEE transactions on electron devices, vol 46., no 10, oct 1999, p. 2035-9

** http://esapub.esrin.esa.it/pff/pffv8n1/martv8n1.htm

Applications

- Chemical and biological sensors
- Bio-compatibility, e.g. Bone growth applications
- Wafer Bonding capability
  - Control of pore size and depth for Si hydrophilic wafer bonding?



Tiny particles of porous silicon can be used as sensitive detectors. For example, copper ions (Cu2+) bound to the porous silicon could react in the presence of chemical warfare agent Sarin (GF), producing hydrofluoric acid (HF).

http://oemagazine.com/fromTheMagazine/mar03/silicon.html

Summary

- PS has a lot of potential but also needs more work to understand the etching chemistry.
  - CMOS compatible + cheap to make
  - May extend bulk Si as a good OE material
  - Highly controllable, but sensitive features
  - Low dimensionality features make it interesting with exotic properties w.r.t. bulk Si
  - Highly reactive but has aging effects which need to be stabilized.

References

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[8] M.I.J. Beale, J.D. Benjamin, M.J. Uren, N.G. Chew, and A.G. Cullis, J. Cryst. Growth 73, 622 (1985)