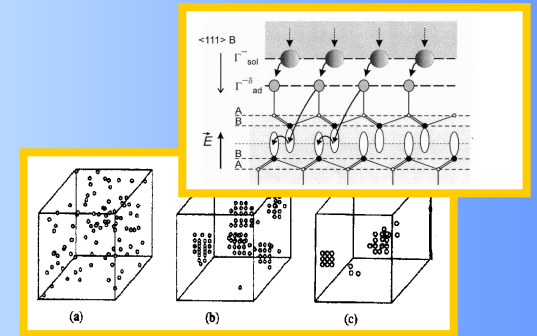
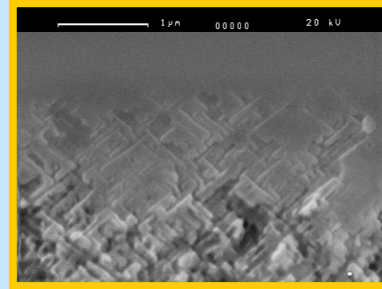


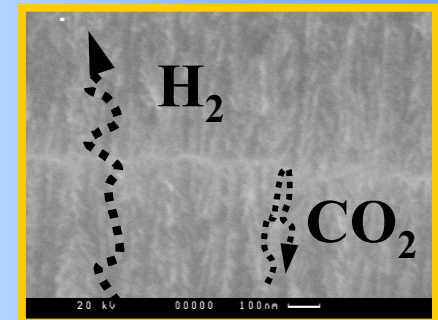
«10 нм полупроводниковые мембраны для очистки водорода»



2005 - Исследования :
 2004 – от технологии до
 2006 – к Производству

$$V \approx \frac{\Delta T}{T} \left(\frac{a}{\lambda} \right)^2 a v \frac{\Delta H}{kT_{ml}} \exp\left(-\frac{\Delta H + AD}{kT_{ml}} \right) \exp\left(-\frac{E}{kT} \right)$$

2006 – от технологии Si мембран
 2007 – к Производству



Принципиальная схема топливного элемента

Электрический ток

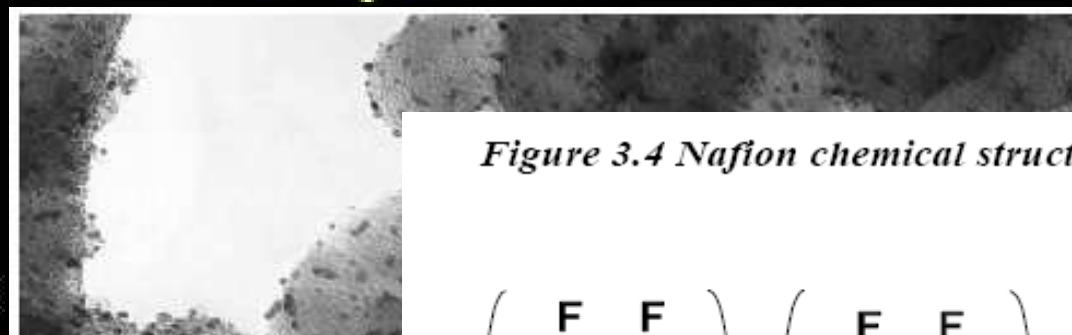


Figure 3.4 Nafion chemical structure

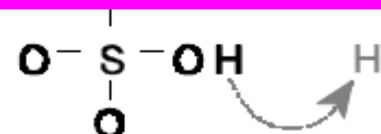
Топливо H_2 (Водород)



Главная проблема - Грязный водород
отравляет катализатор

Необходима Мембрана для
очистки !!??

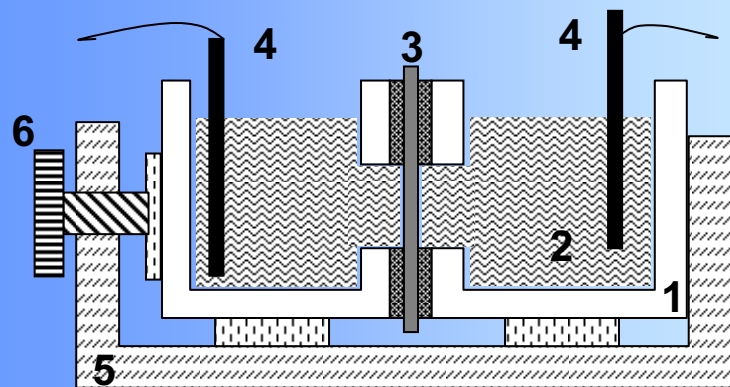
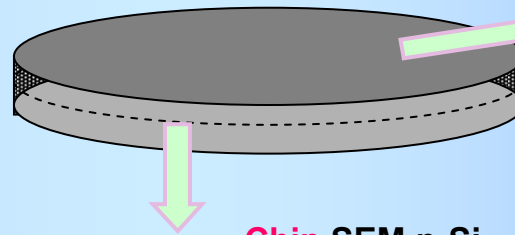
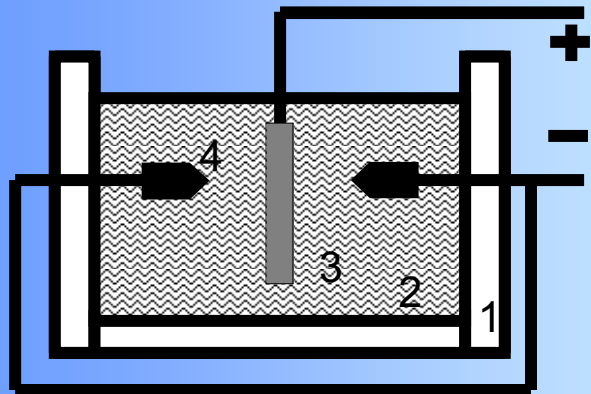
СХЕМА ТВЕРДО



Technology : – electrolytic pore-formation of semiconductor, solid layer in the middle of porous substrate

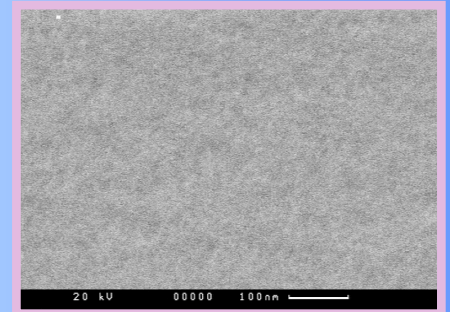
$$\text{Permeability: } Q = \frac{\rho \varepsilon}{L} D_0(q) K_0 \exp\left(\frac{\Delta H_a}{RT}\right) \exp\left(-\frac{\Delta E}{RT}\right) = Q_0 \exp\left(\frac{\Delta H_a - \Delta E}{RT}\right)$$

L- membrane thickness

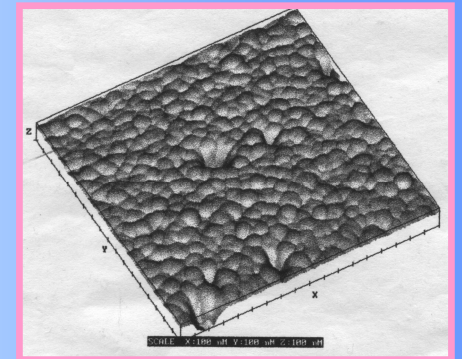


Electrolytic cells: top – simple sell, bottom- advanced cell.
 1 – teflon cell, 2 – electrolyte solution, 3 – Si substrate,
 4- electrodes, 5- cell frame, 6 – compressive screw

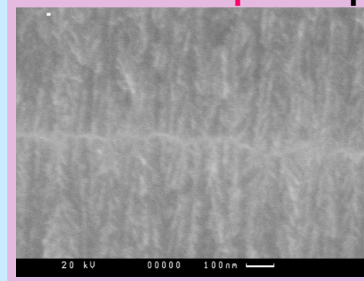
Surface SEM p-Si



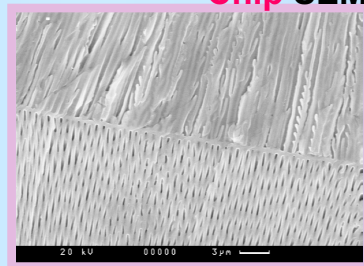
Surface AFM p-Si



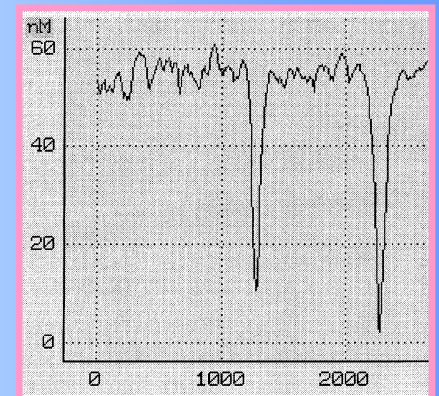
Chip SEM p-Si



Chip SEM n-GaP



Surface AFM depth profile p-Si



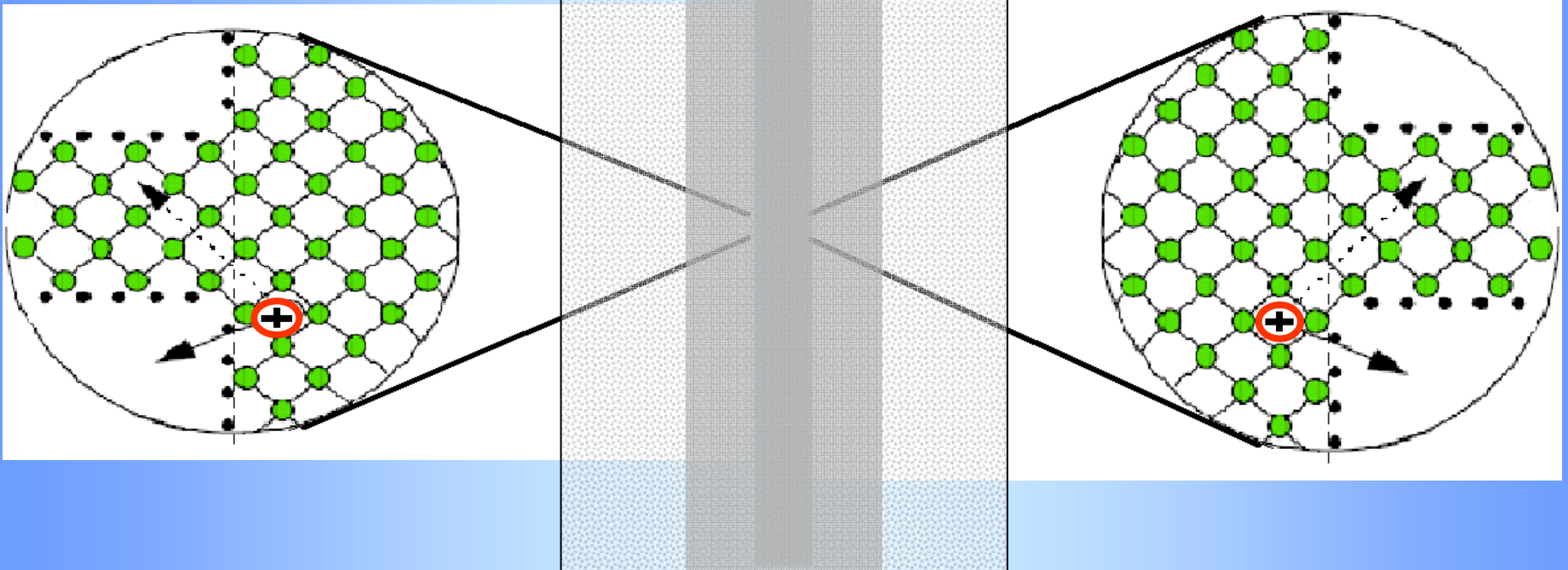
Porous layer

Solid layer

Debye length – no free charge carriers

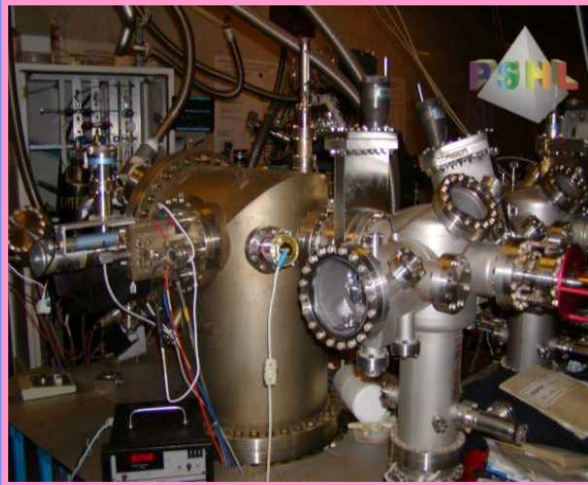
$$\delta = (8 \cdot \epsilon \cdot \epsilon_0 \cdot \Delta\phi_{sc} / e \cdot N)^{1/2}$$

For $N = 2 \cdot 10^{19} \text{ cm}^{-3}$, $\delta = 8.6 \text{ nm}$

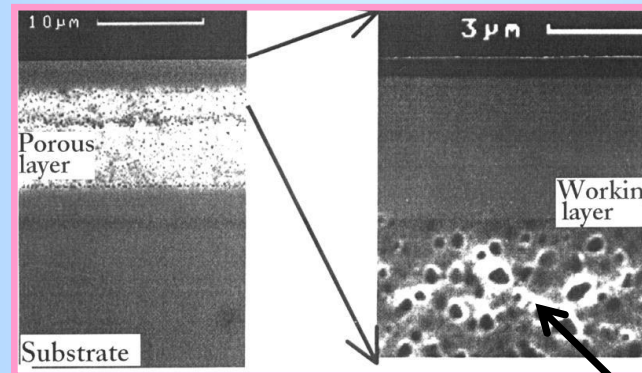


Technology : – electrolytic pore-formation of semiconductor, solid layer and whiskers on porous substrate

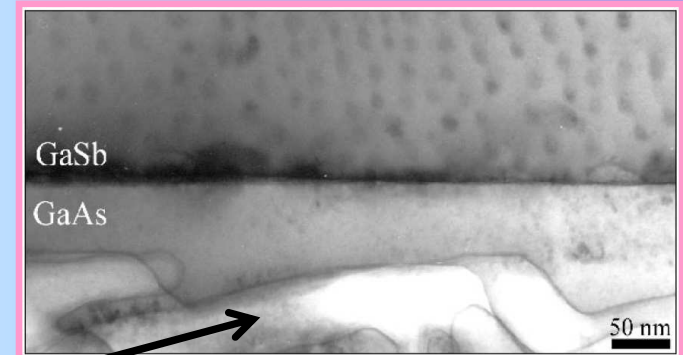
A.V. Bobyl, S.G. Konnikov, V.P. Ulin et al.



Chip SEM homoepitaxy InP on InP



Chip TEM strained heteroepitaxy GaSb on GaAs

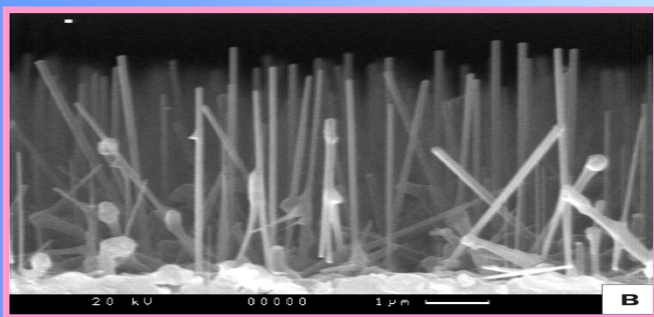


Pores

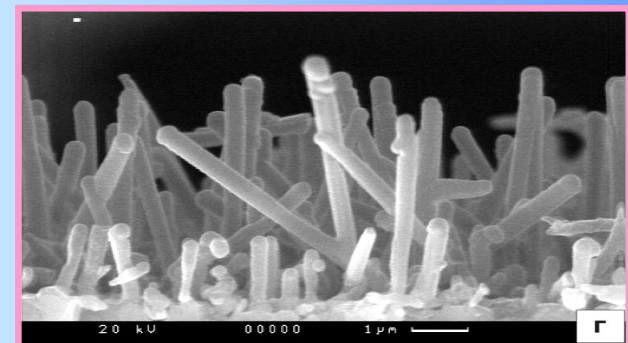
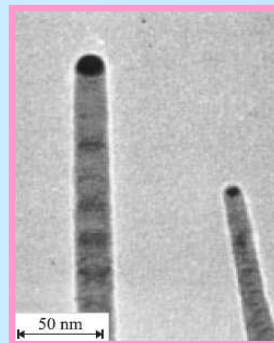
Molecular beam epitaxy

V. G. Dubrovskii, G. E. Cirilin, Yu. B. Samsonenko, V. M. Ustinov et al.

Surface SEM 10 nm GaAs whiskers

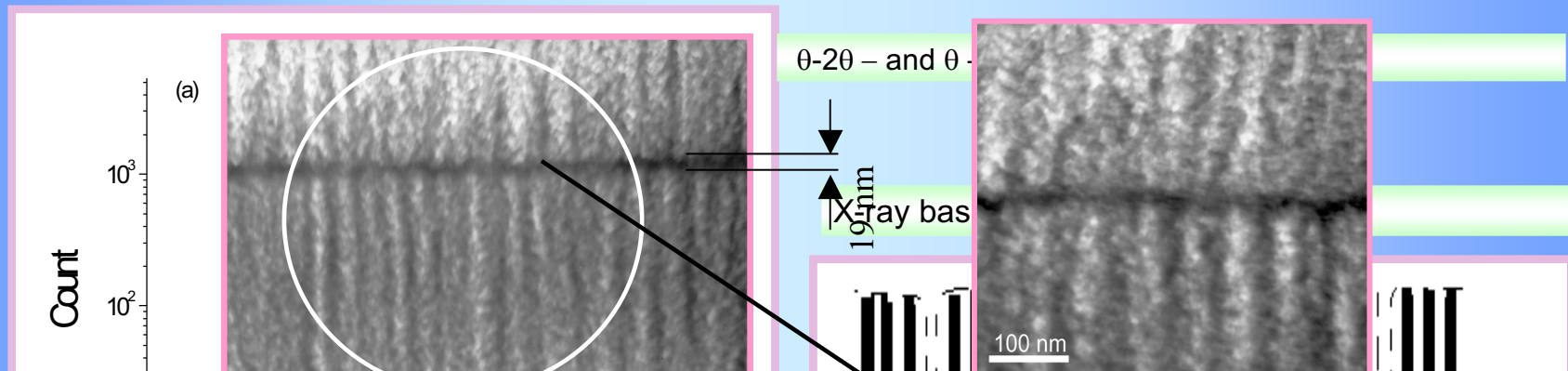


Surface SEM 10 nm GaAs whiskers cupped and covered by metal



Investigation : - structural : X – ray and TEM

X-ray diffraction Transmission electron microscopy

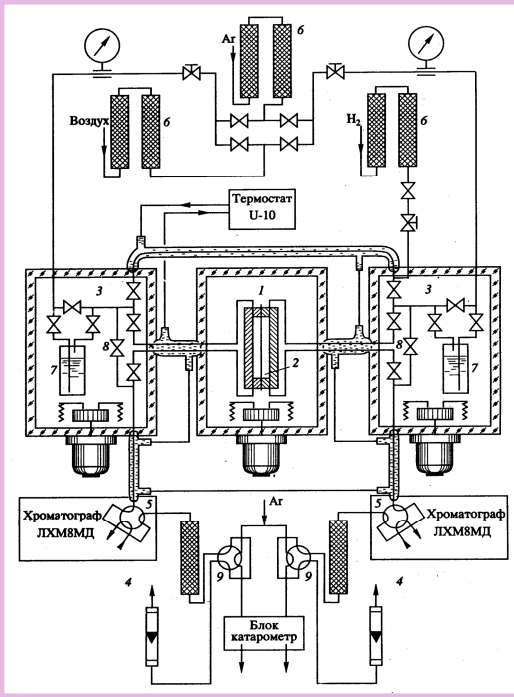


**Сплошной слой имеет высокое
качество поскольку является
монокристаллом**

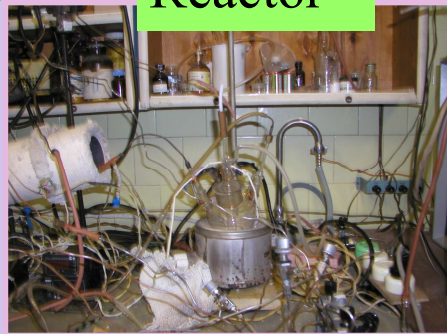
crystal-like diffraction

Исследование проницаемости и селективности

High-precision gas-analyser



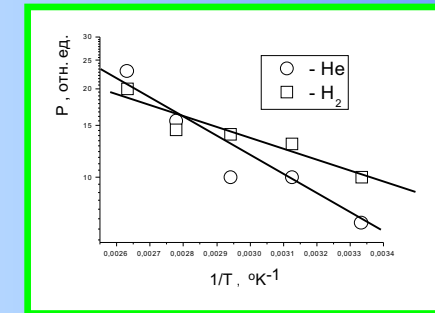
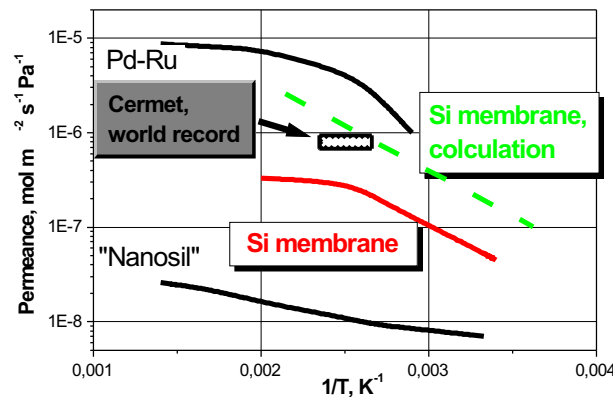
Reactor



Registration system



Membrane



Activation energy for **He** approximately two times bigger than for **H₂**.

	Hydrogen permeability [mol/m ² s Pa]x10 ⁻¹⁰		Activation energy, eV	Substrate orientation	Substrate resistance, Ω cm	Debai length, nm
	300 K	500 K				
Si-2	2.01	6.70	0.092	(111)	0.02	~ 8.5
Si-3	3.93	49.7	0.18	(100)	0.01	~ 6.0

Debai length

$$\delta = (8 \cdot \varepsilon \cdot \varepsilon_0 \cdot \Delta\varphi_{sc} / e \cdot N)^{1/2}$$

For $N = 2 \cdot 10^{19} \text{ cm}^{-3}$,

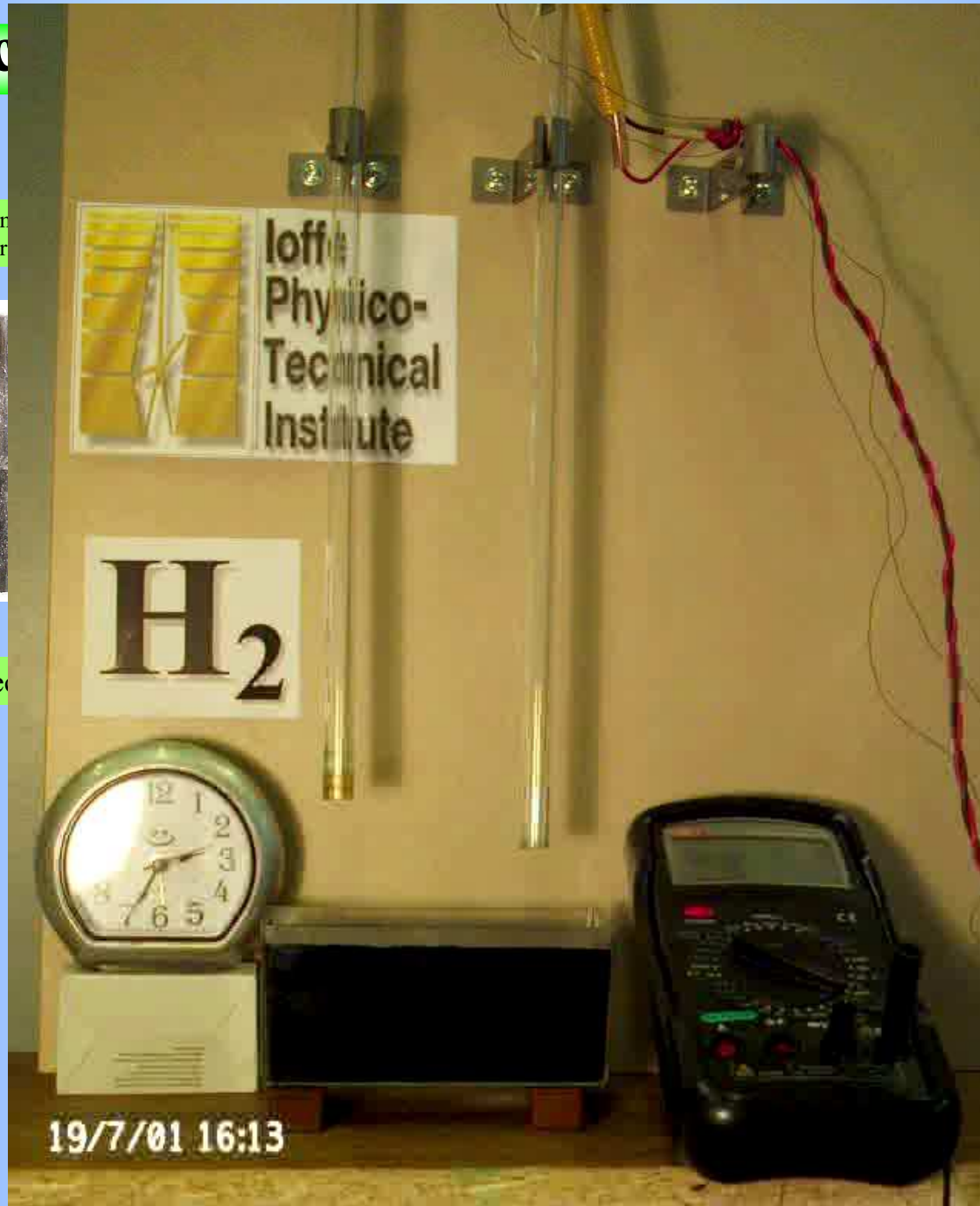
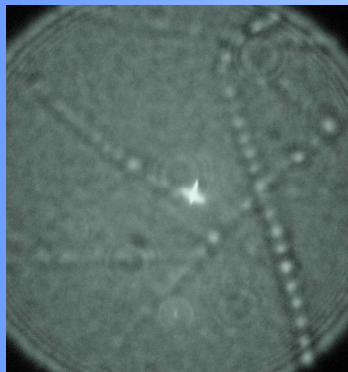
$$\delta = 8.6 \text{ nm}$$

Экспресс

Optical IR images of mesoporous Si substrate (20x20 mm²). Left and r



Undesirable membrane defe



Продности

Overview



8. Levels in 120 min at room and 80 C temperatures

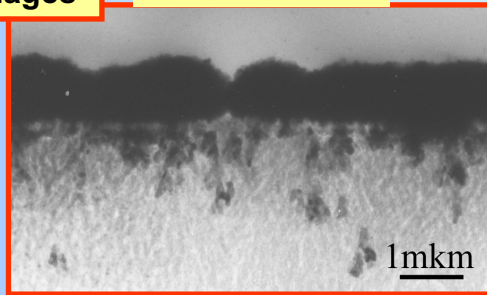
Application: – problems of thermal stability and mechanical strength

Pd on solid Si

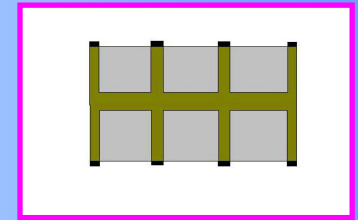
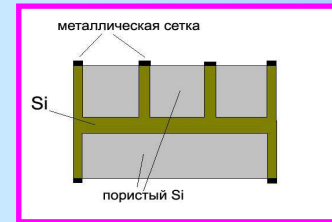


TEM images

Pd on porous Si

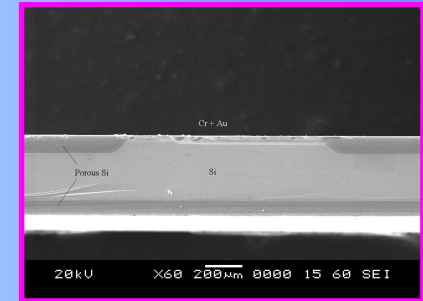
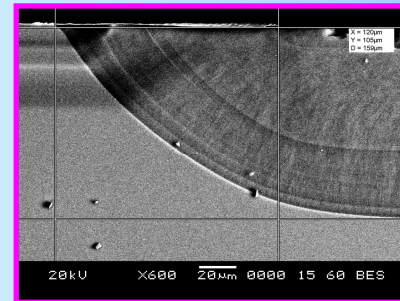
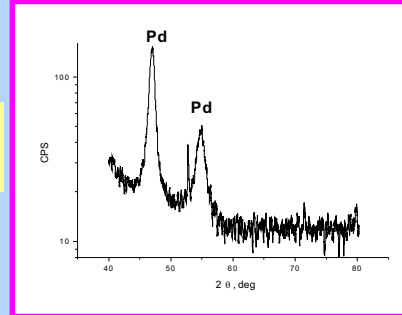
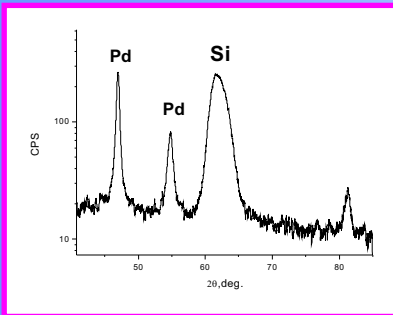


armored coating of porous Si

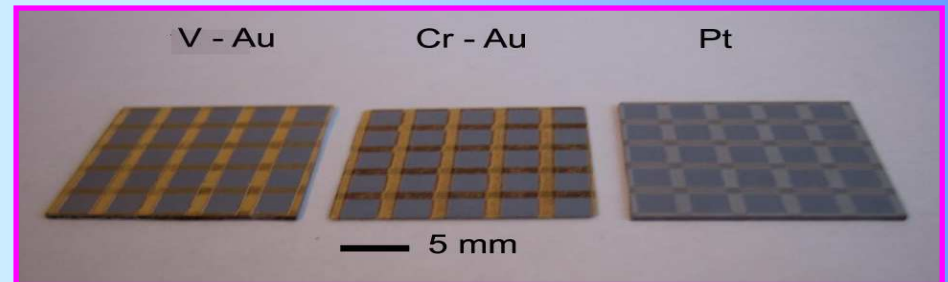
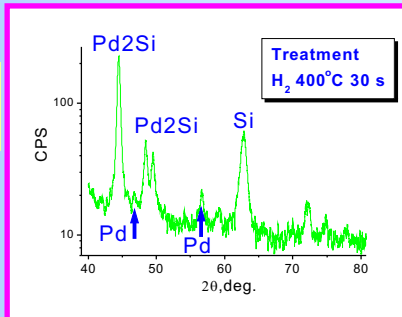
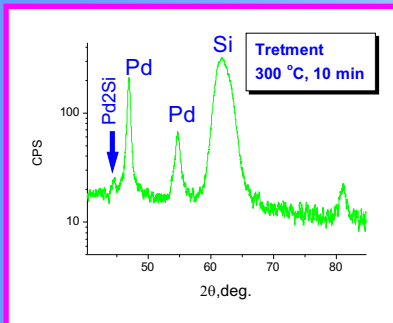


X - ray

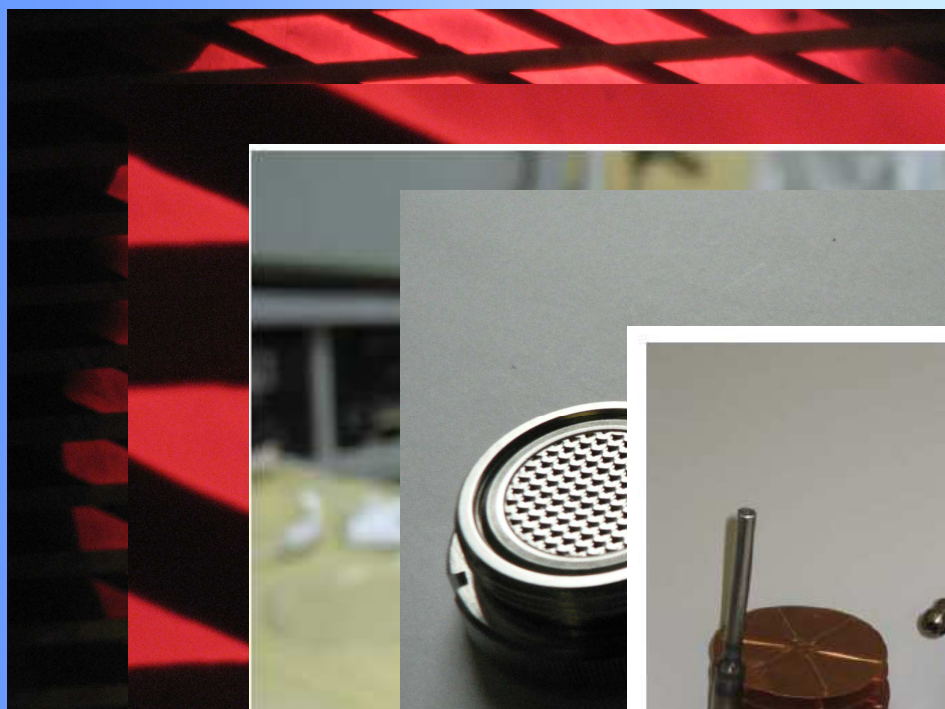
Before treatment



After treatment



Мембраны 2-го поколения

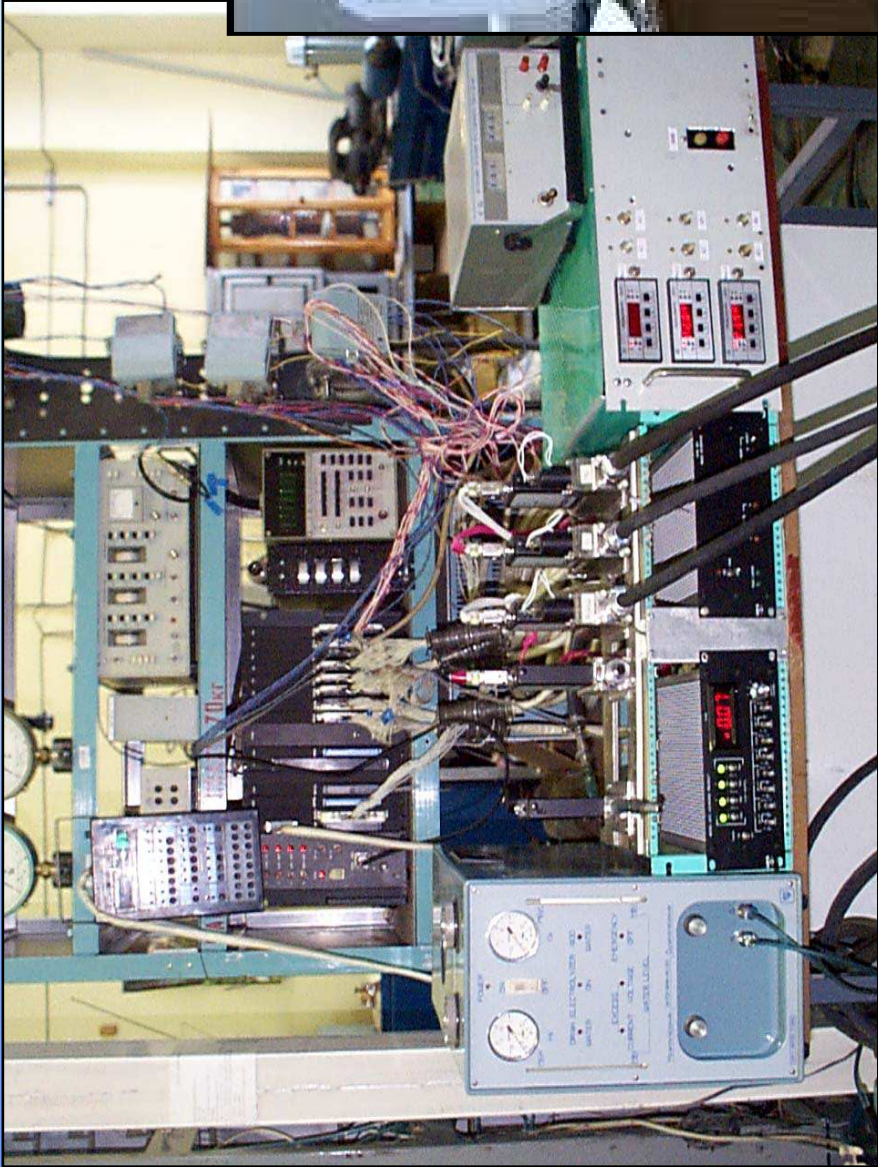


II. Patent RF (utility model) “С

Patent application N 2008148241

Possible lamellar Si membrane modules.
25.10.2008

**Ulin V.P., Soldatenkov F.Y., Bobyl A.V., Chusov A.N., Fedorov M.P.,
Gromova O. B., Tereschenko G.F.**



Выводы:

- 1) Разработана технология высокоселективных **10 нм мембран** с использованием современной полупроводниковой технологии
- 2) Температурная зависимость проницаемости мембран имеет вид закона Аррениуса - **отсутствие микротрещин** центрального сплошного слоя
- 3) Проводимость и **механическая прочность** может быть повышена до величин исходной Si подложки
- 4) Si мембрана обеспечивает очистку водорода для **300 mW/cm²** топливных элементов. Реально пока - **100-mW/cm²** .