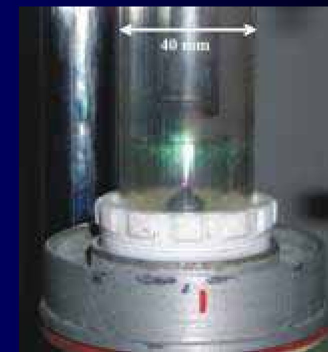
Deposition of carbon nanotubes in microwave torch and their application



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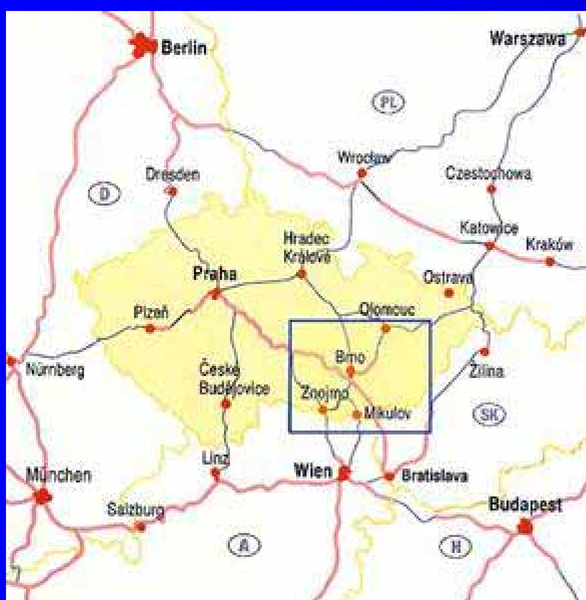
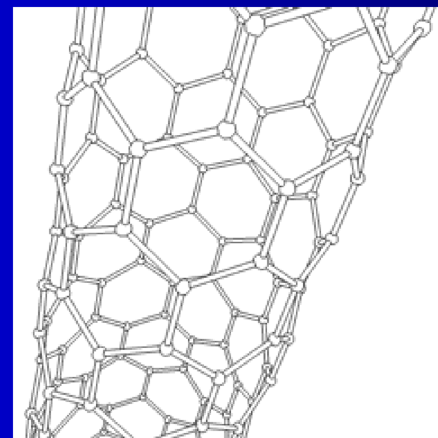


http://www.physics.muni.cz/kfe

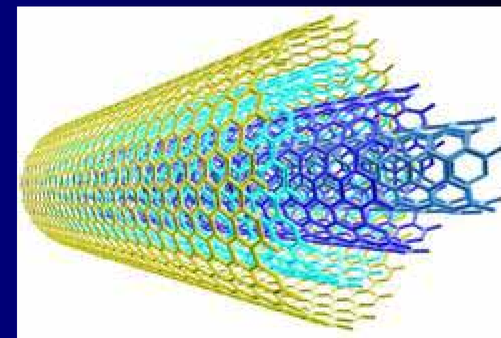
department profile: plasma processing of materials (PECVD, plasma treatment, PVD), plasma physics, hard films, plasma polymers, CNTs, Fe-based nanoparticles, characterization of thin films

Carbon Nanotubes and Their Synthesis

- **arc discharge deposition**
  large quantities of CNTs but the purity is usually about 30%; not suitable for direct synthesis of supported aligned CNTs
- **laser ablation of graphite**
  costly apparatus not amenable for scaleup; small quantities of high-quality SWNTs in 70-90% purity

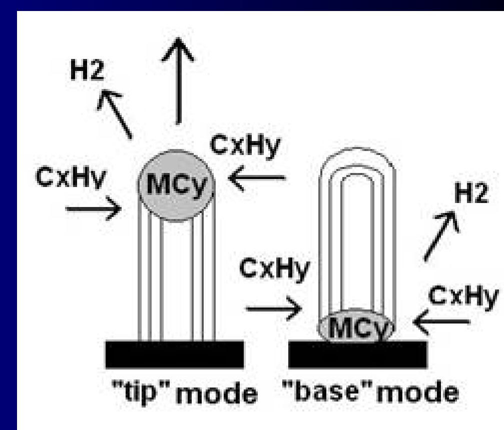


single-walled nanotube (SWNT)



multi-walled nanotube (MWNT)

- **chemical vapor deposition (CVD)** → supported catalyst: Fe, Ni, Co ...



(energy source)

plasma enhanced CVD (PECVD)

thermal CVD

reactants: hydrocarbons or CO mixed with H_2, NH_3, N_2 ...

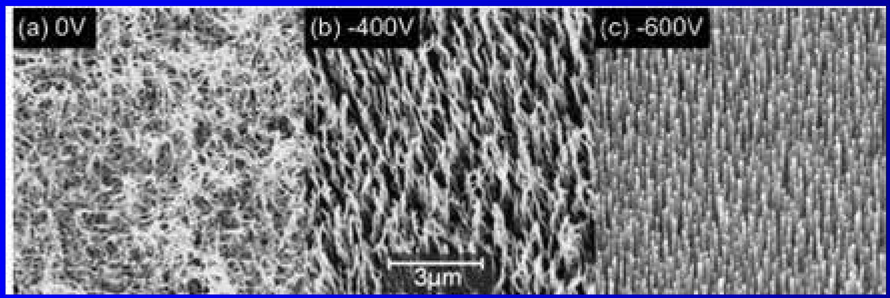
floating catalyst: $Fe(C_5H_5)_2$, $Fe(CO)_5$

Chemical Vapor Deposition of CNTs

method for direct synthesis of supported aligned CNTs ⇒ widely used in recent years

- thermal CVD versus PECVD:

widely accepted argument for PECVD – the presence of inherent electric field influencing the growth orientation of CNTs



Chhowalla et al., J. Appl. Phys. 90, (2001), 5308

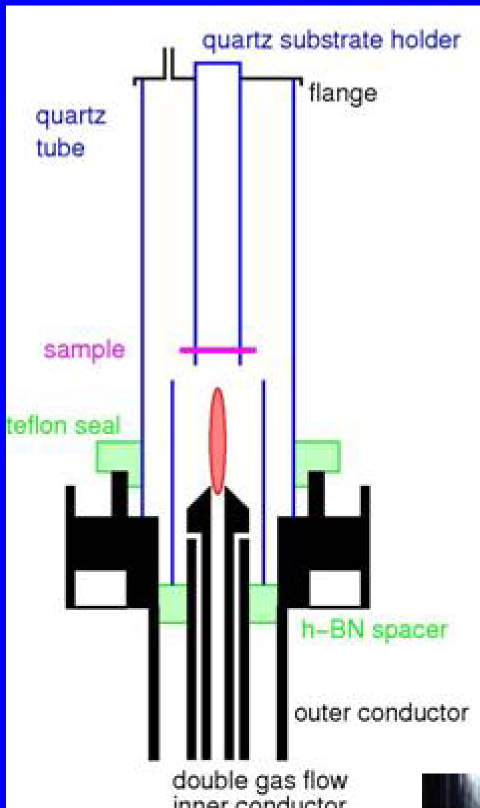
conventional argument ?? - lower process temperature of PECVD

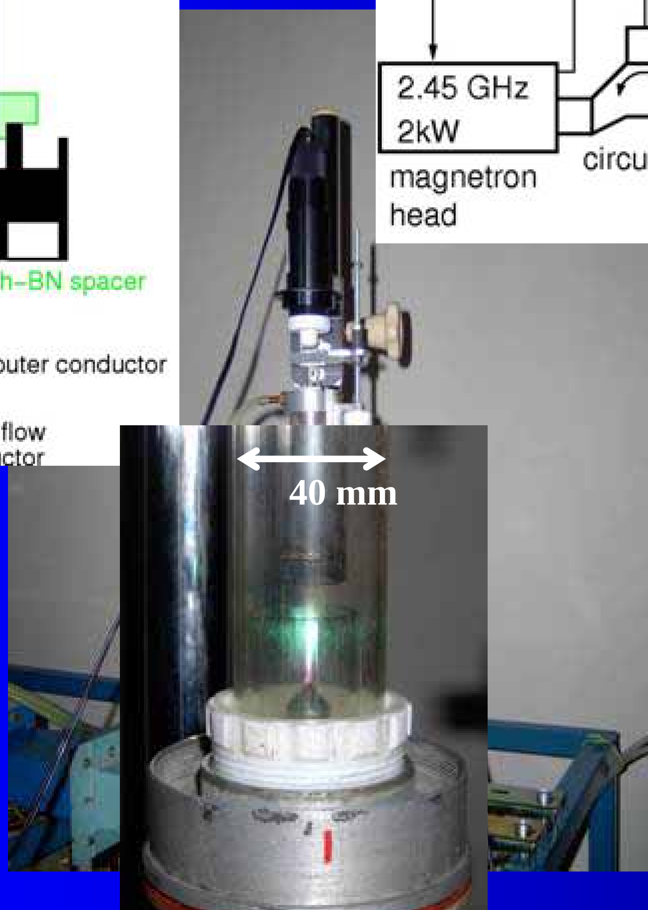
- low pressure PECVD: d.c. and r.f. glow discharges, microwave discharge, ECR, ...

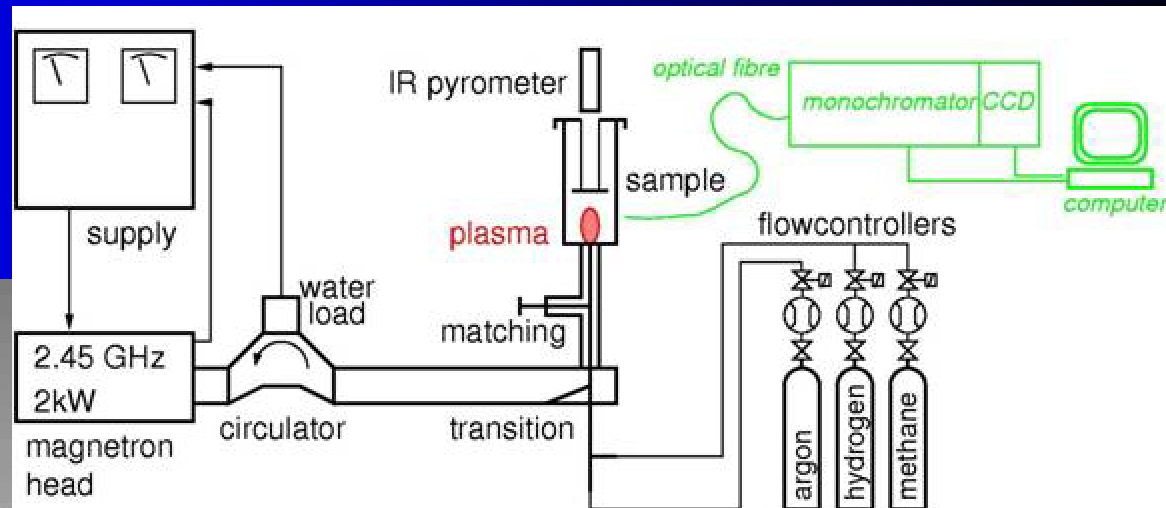
- atmospheric pressure PECVD: DBD, APG, torches and jets

unique approach - surface bound deposition of CNTs by PECVD in microwave torch

Microwave Torch at Atmospheric Pressure for Deposition of CNTs







- frequency of 2.45 GHz
- dual gas flow injection: central Ar flow and sidewall flow of CH_4/H_2
- supported or floating catalyst approach
- substrate temperature measured by pyrometer

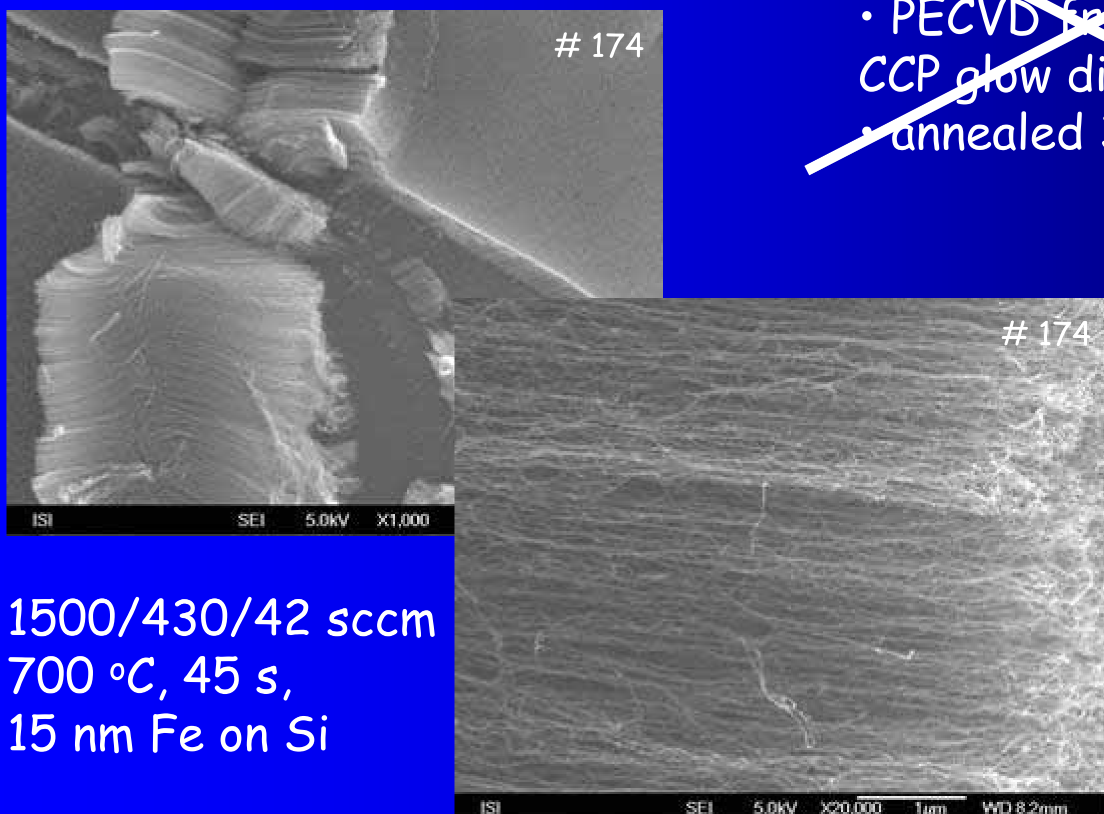
Surface-Bound Deposition of CNTs in MW Torch

- mw power: 400 W
- Ar: 1500 sccm
- H_2: 285-430 sccm
- CH_4: 25-42 sccm

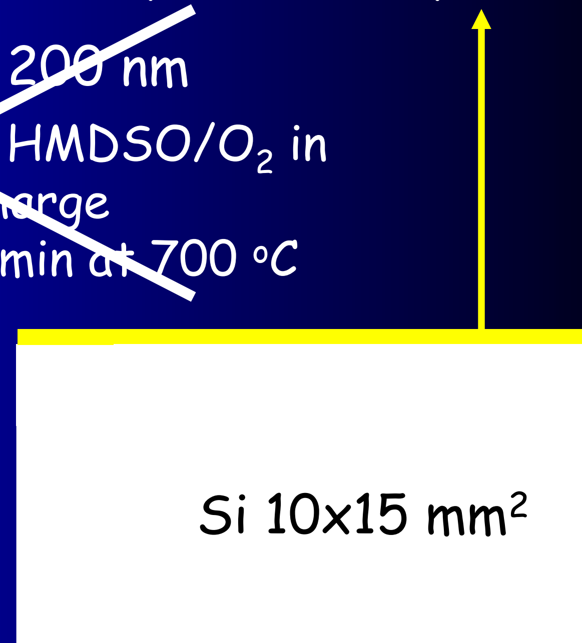
- barrier diffusion layer ISN'T NECESSARY!

Fe catalytic layer, 2-20 nm
- prepared by vacuum evaporation

SiO_2-like film, 200 nm
- PECVD from HMDSO/O_2 in CCP glow discharge
- annealed 30 min at 700 °C



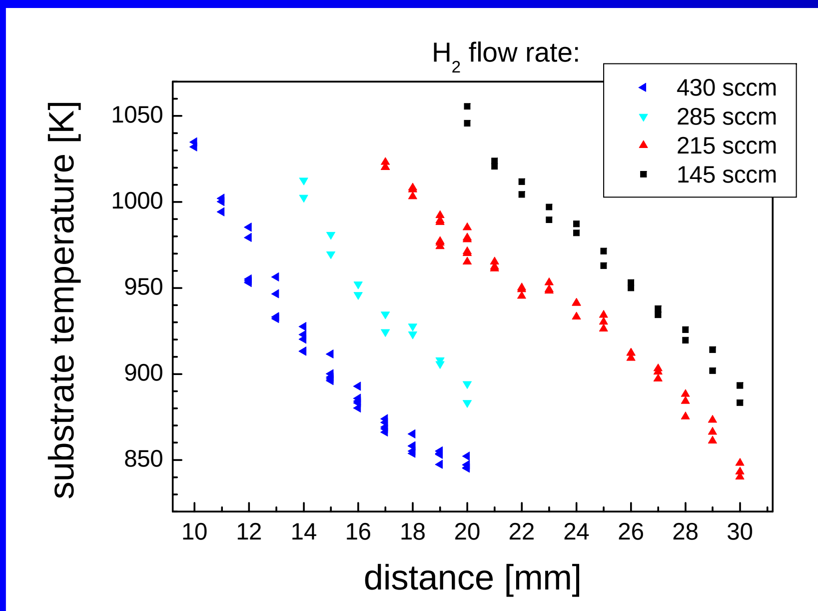
1500/430/42 sccm
700 °C, 45 s,
15 nm Fe on Si



Control of Substrate Temperature

substrate is heated by heat exchange with the gas and surface recombination

gas temperature is controlled by
power input, gas mixture, spatial position



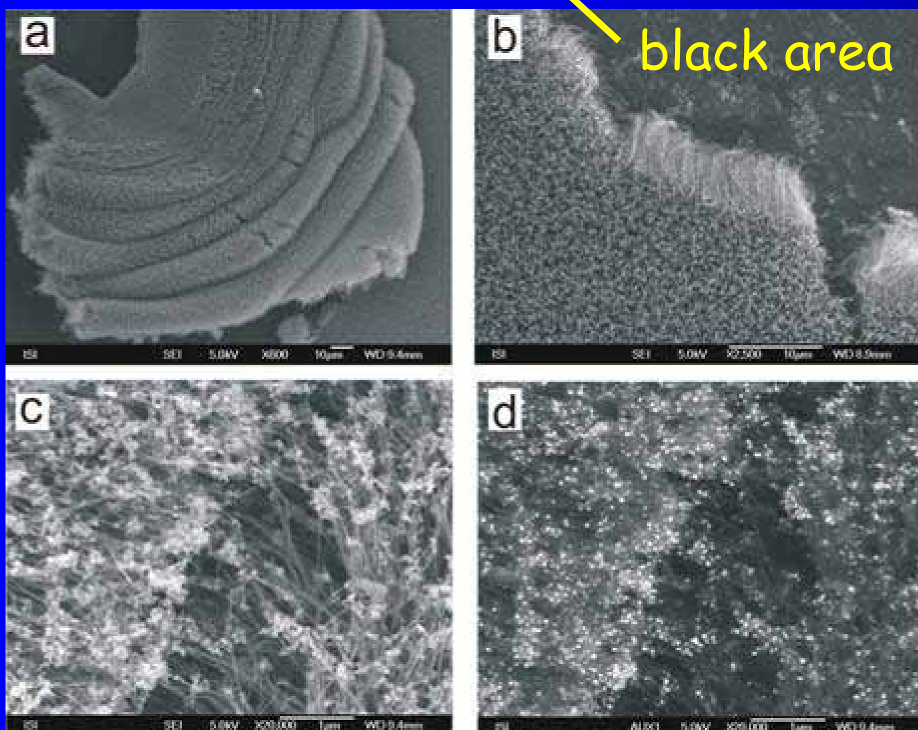
Ar/H_2/CH_4
T_{rot} = 3100-3900 K
T_{subs} > 770 K

400 W, 1500 sccm of Ar, 42 sccm of CH_4

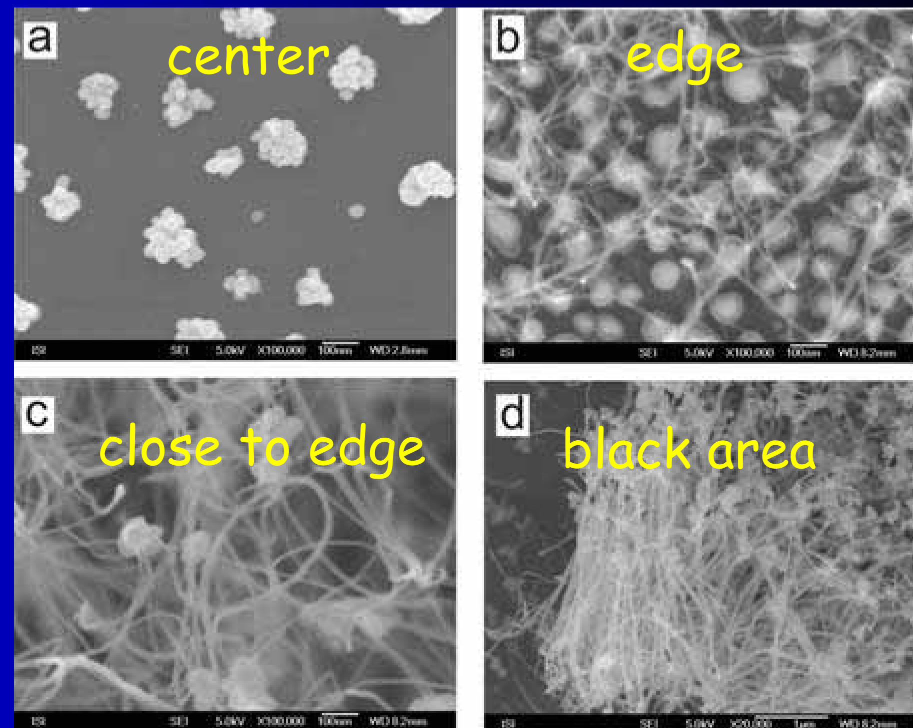
L. Zajíčková et al. Plasma Phys. Control. Fusion 47 (2005) B655

Characterization of Deposited CNTs I.

problem of non-uniformity ⇔ small diameter of the torch: (i) gradients of reactive species, (ii) non-uniform substrate heating



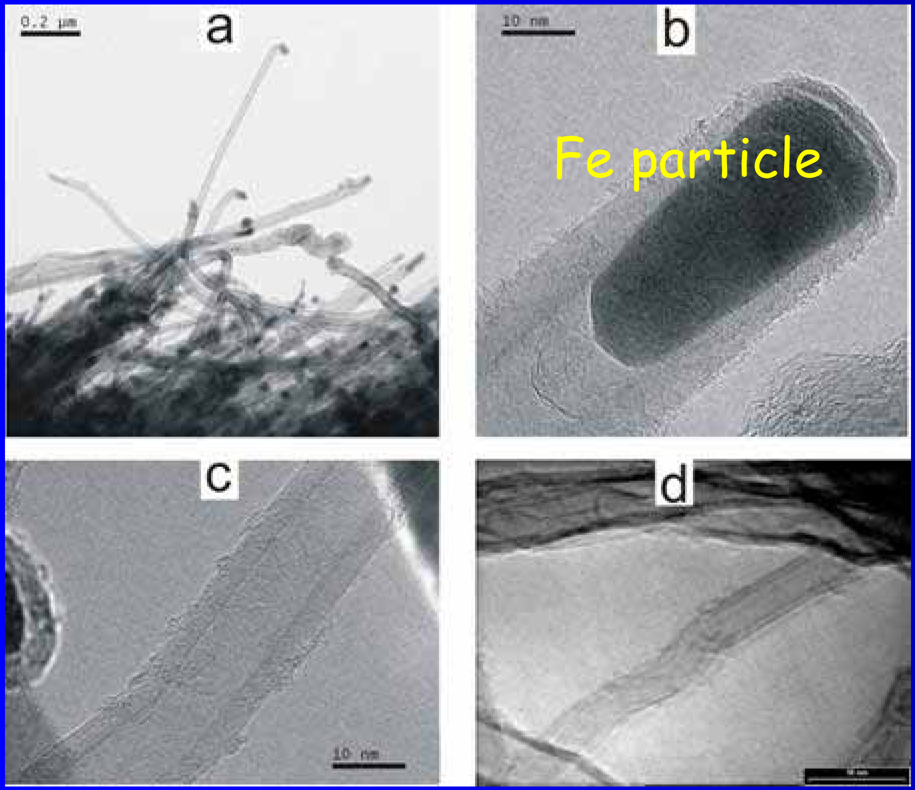
1500/430/42 sccm of $Ar/H_2/CH_4$

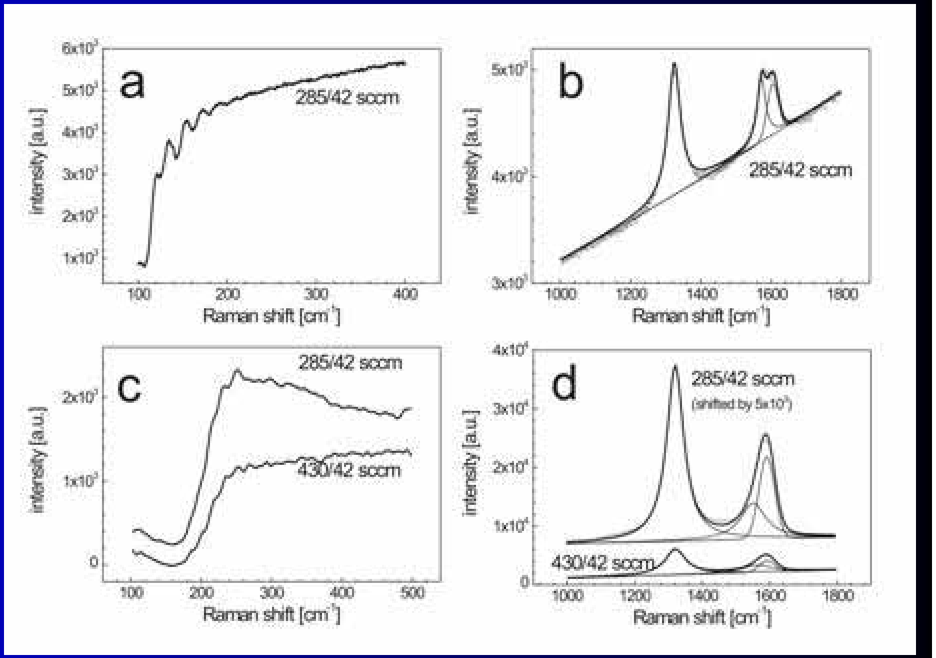


1500/285/42 sccm of $Ar/H_2/CH_4$

L. Zajíčková et al. Plasma Process. Polymers 4 (2007) S245

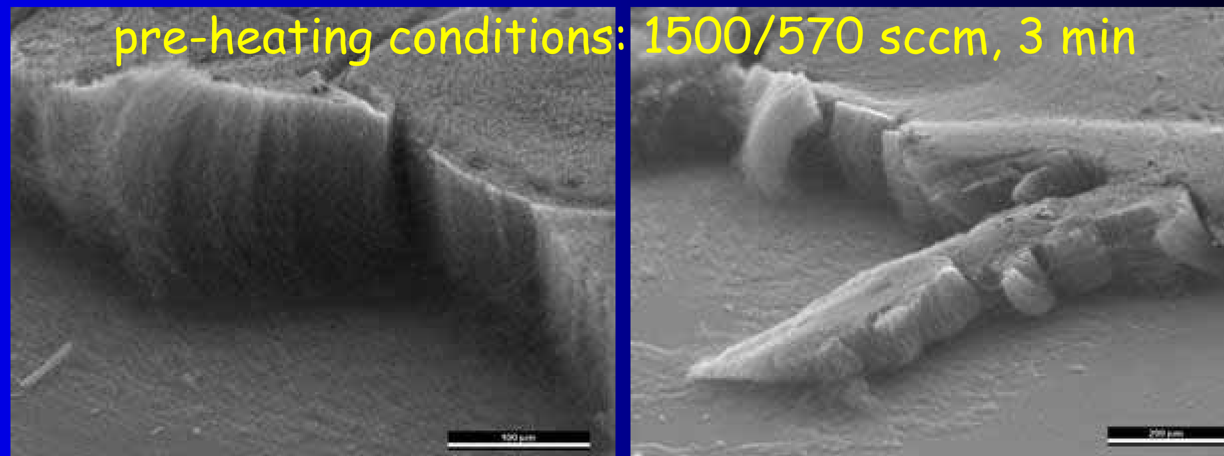
Characterization of Deposited CNTs II.





Some Ways to Improve Deposition Uniformity

- pre-heating of the substrate in Ar/H_2 torch



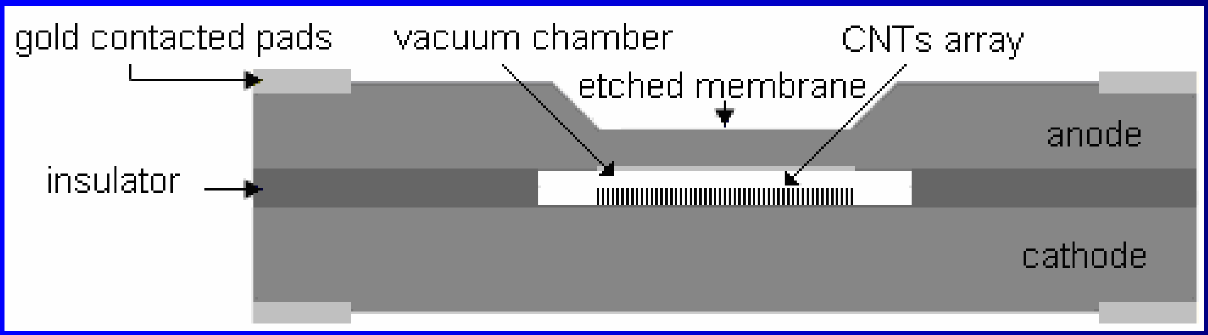
O. Jašek et al. J. Phys. Chem. Solids 68 (2007) 738

- flipping the catalytical active layer outwards the torch

  The active area for the CNT deposition IS NOT in a direct contact with the torch and the uniformity is influenced only by the gas flow

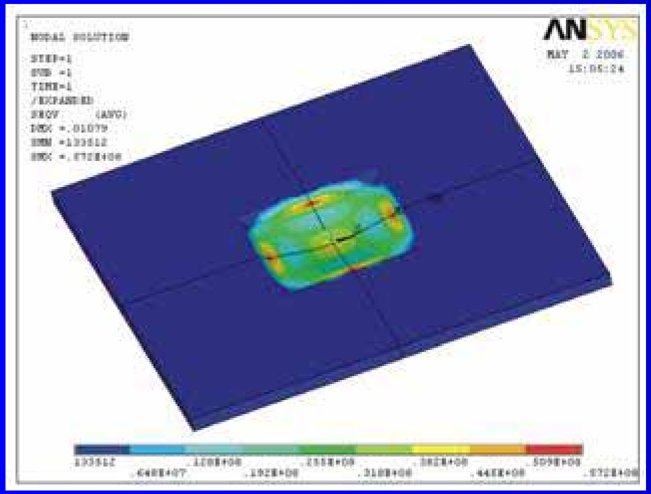
- larger uniform areas - moveable torch or substrate, multi-torch operation ?

Pressure Sensor Based on Field Emission of CNTs



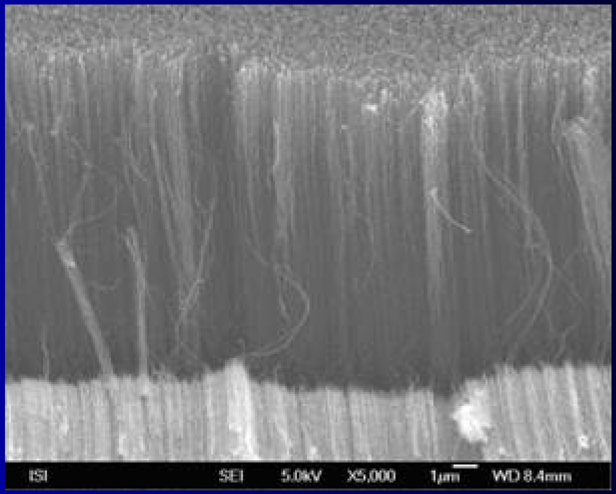
fabricated using
- 525 μm thick Si doped to 0.005 Ωcm
- insulating spacer
- directly deposited CNTs

anode – silicon membrane etched anisotropically in KOH solution



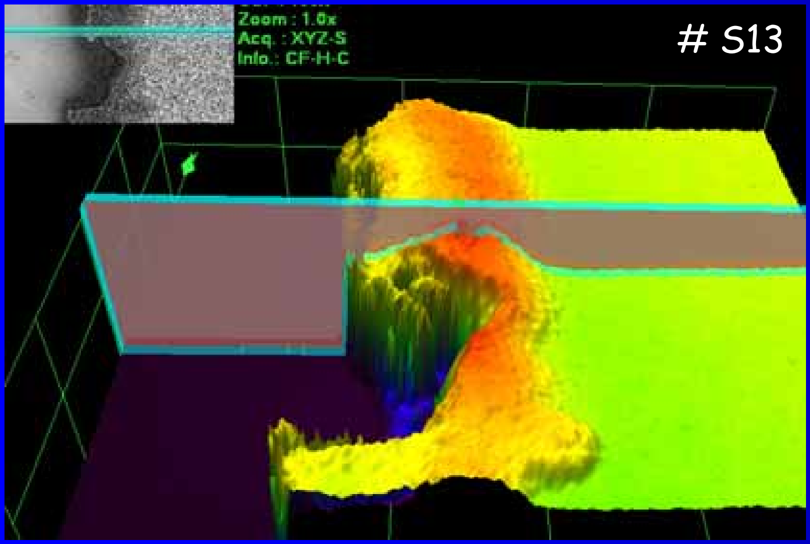
Simulation of deflection and stresses by ANSYS ⇒ area and thickness optimization for 0-500 kPa (shown for 100 kPa)

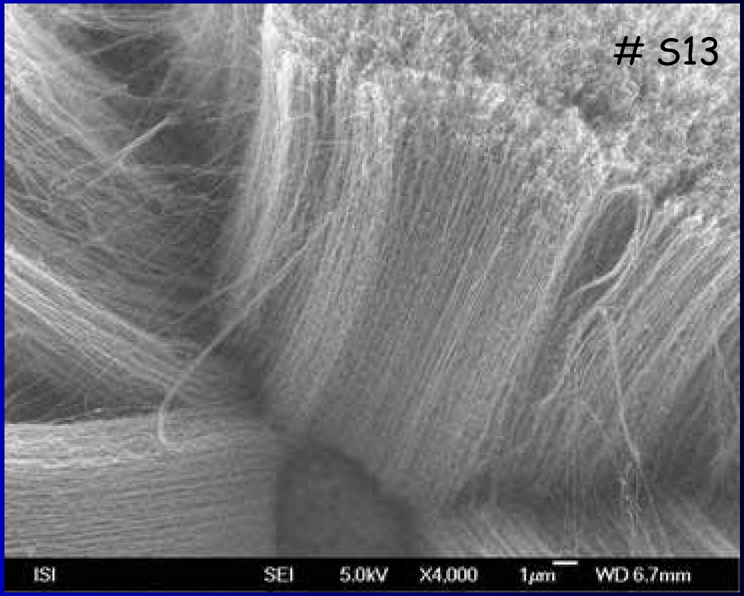
cathode – emitting CNTs on conductive Si



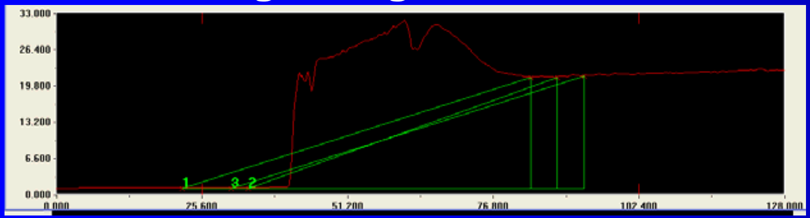
are of 5 x 5 mm, thickness of 200 μm

Pressure Sensor Based on Field Emission of CNTs

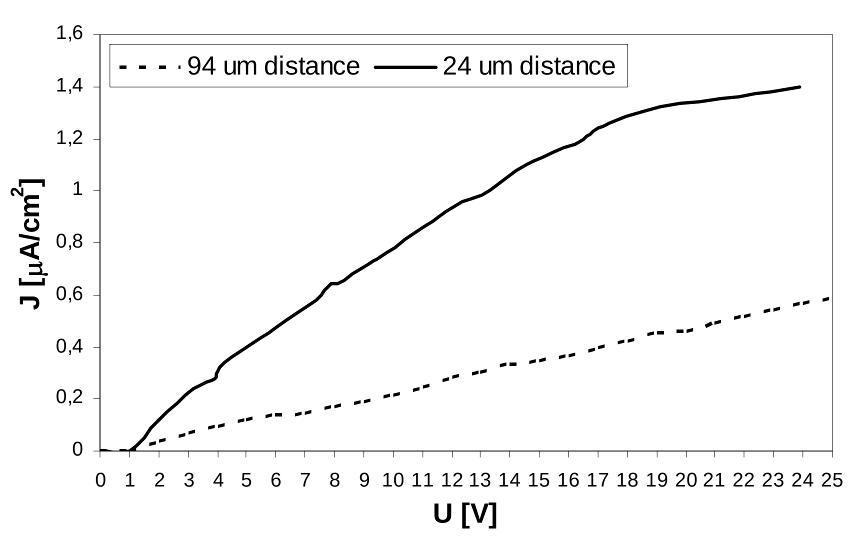




average height of 20 μm



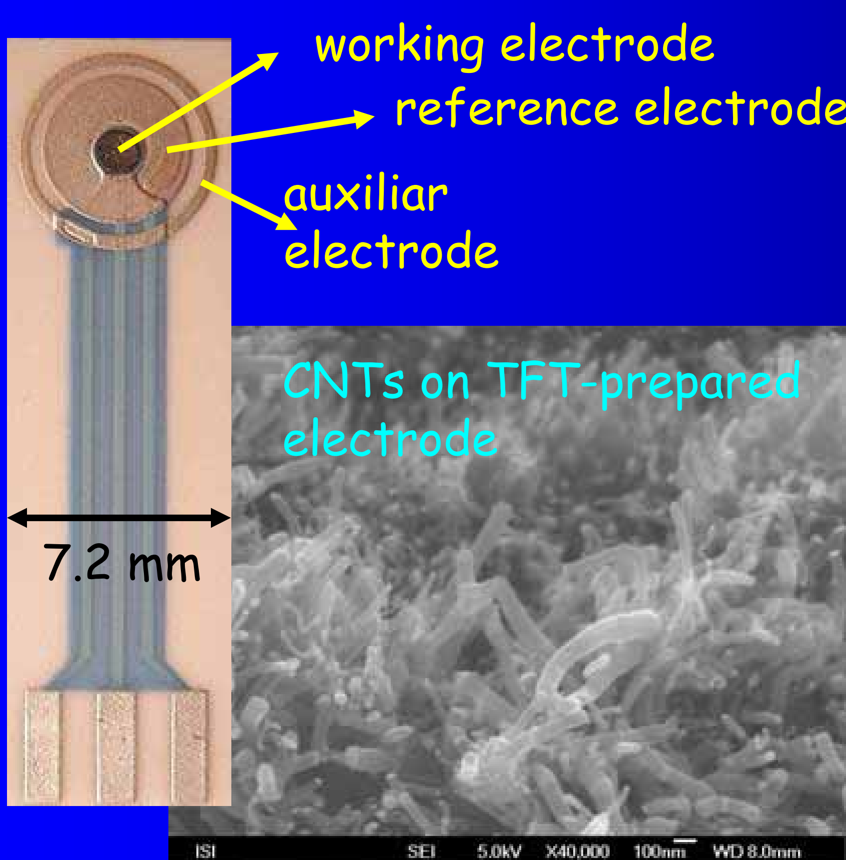
1500/430/42 sccm
700 °C, 30 s – treatm. + 30 s – depos.
15 nm Fe on Si

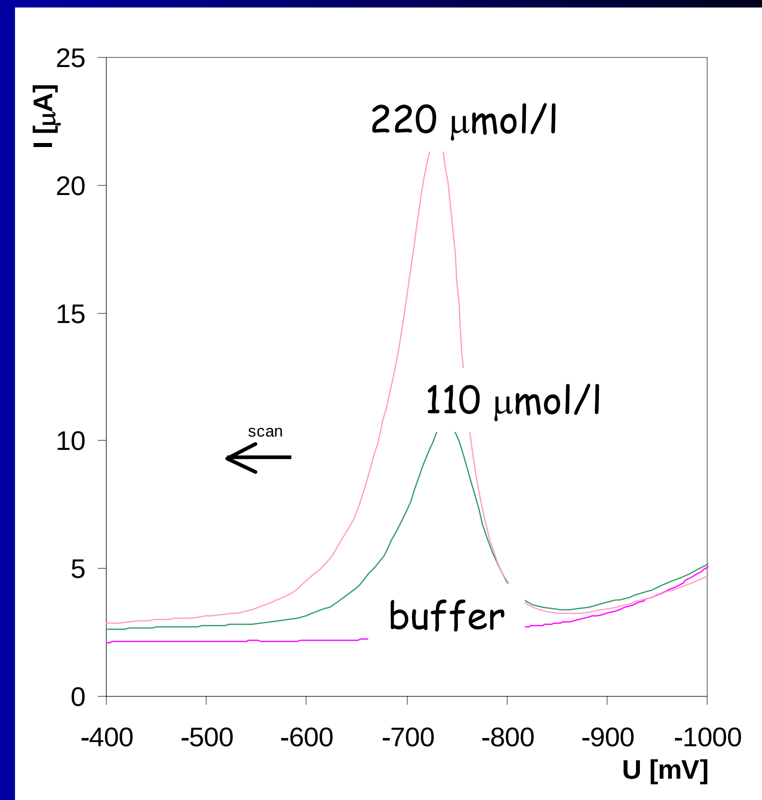


Heavy Metal Sensor: Electrochemical Detection

electrochemistry is suitable technique for detection of heavy metals but it is necessary to replace Hg electrodes ⇒ sensors with solid electrodes prepared by Thick Film Technology (screen-printing),

area increase required! → CNTs





detection of cadmium in KCL by differential pulsed voltammetry

Conclusion

- Microwave torch used for the deposition of CNTs at atmospheric pressure has several pros and cons:

- without requirement of vacuum and heating equipment

- fast process time: catalyst activation is an integral part of the deposition, deposition of 20 μm long CNTs within 30 s

- problem of reproducibility due to high speed of the process

- problem of non-uniformity

- The process can be applied for the preparation of functional devices such as sensors based on the emissive properties, electrode area increase or perhaps electrical resistance of CNTs.