CO VYČTEME ZE SVĚTLA?

Mgr. Zdeněk Remeš, PhD.

Mýtus je předchůdcem umění i vědy (Jan Sokol)

Vědecká revoluce 17-tého století

- Autorita není důkaz
- Tradice není důkaz
- „selský rozum“ není důkaz
- Filosofická spekulace není důkaz

Pouze naměřená data získaná kritickým pozorováním
nebo experimentálně mohou
dokázat nebo vyvrátit vědeckou teorii

Galileo Galilei (1564 – 1642)

Rychlost světla

Proč Galileo nebyl schopen změřit rychlost světla?

Duha = sluneční spektrum

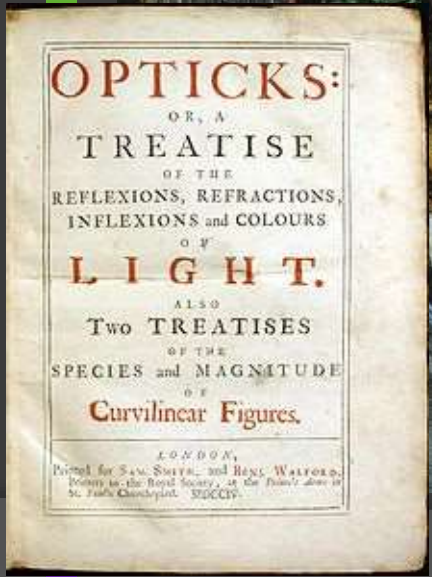
1595-1667

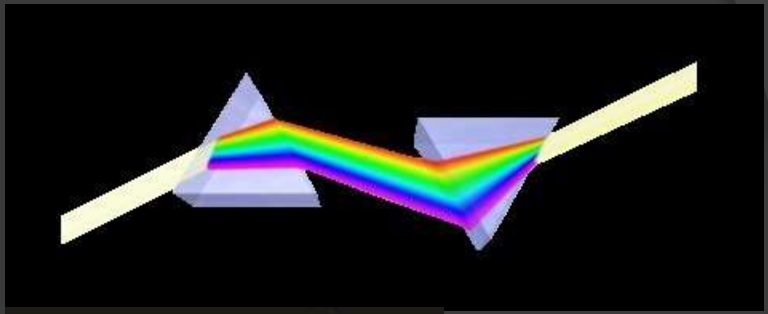
Jan Marek Marci: *Thaumantias. Liber de arcu coelesti deque colorum apparentium natura, ortu et causis* (Praha, 1648)

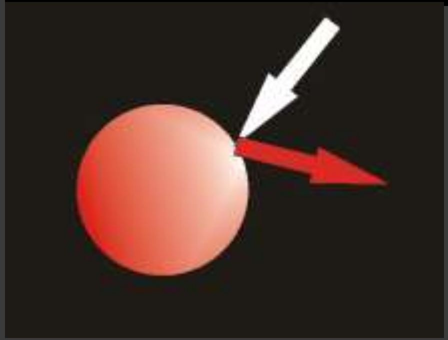
Spektroskopická společnost Jana Marka Marci
http://www.spektroskopie.cz

Isaac Newton (1642 – 1727)

Newtonova teorie barev (1704)

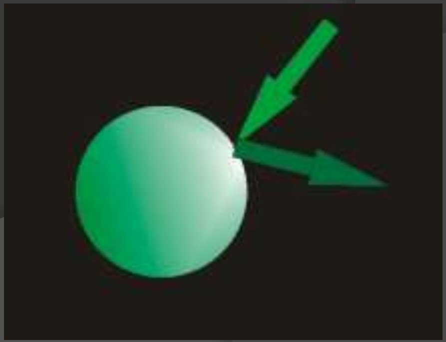

OPTICKS:
OR, A
TREATISE
OF THE
REFLEXIONS, REFRACTIONS, INFLEXIONS and COLOURS
OF
LIGHT.
ALSO
Two TREATISES
OF THE
SPECIES and MAGNITUDE
OF
Curvilinear Figures.
LONDON,





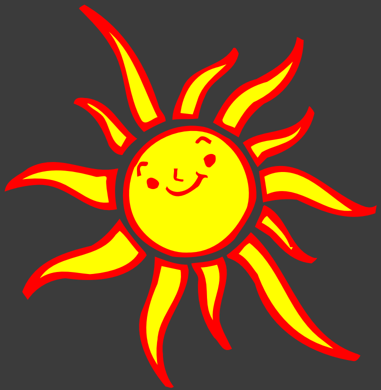
Proč jsou předměty různobarevné v bílem světle?

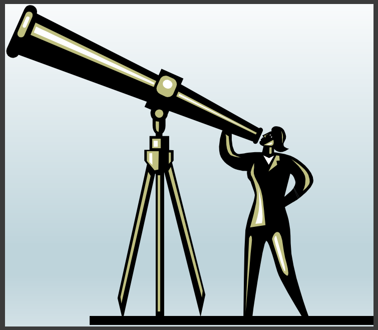
Jak vypadají předměty v monochromatickém světle?

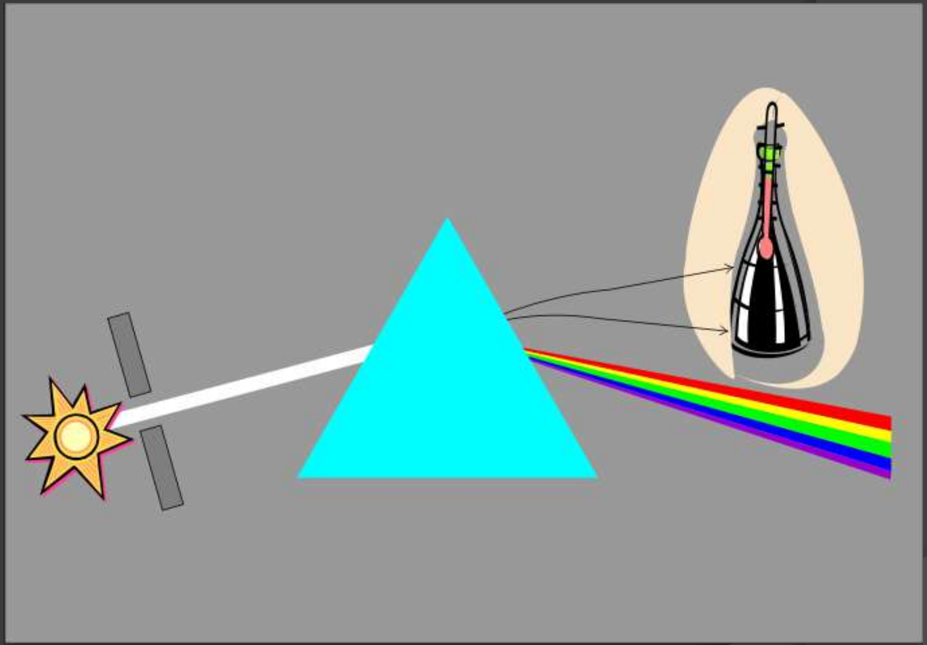


William Herschel (1738 – 1822)

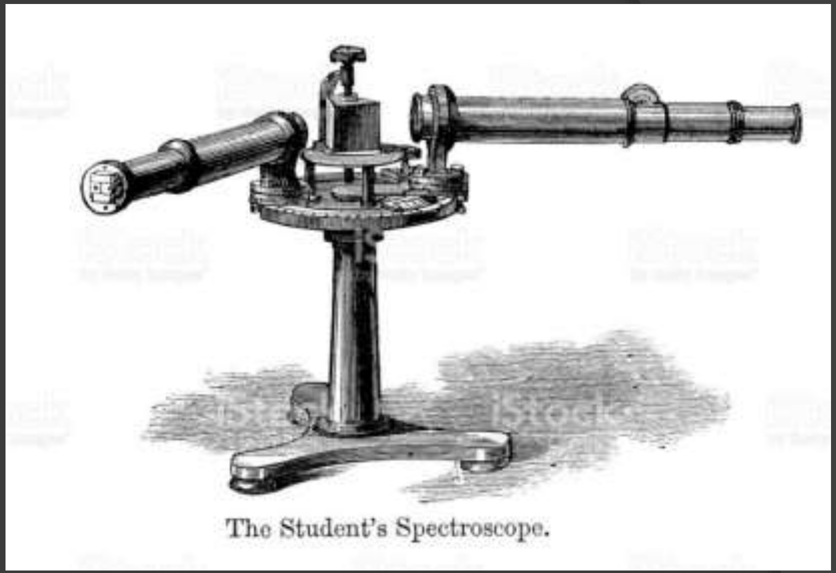
Infračervené světlo

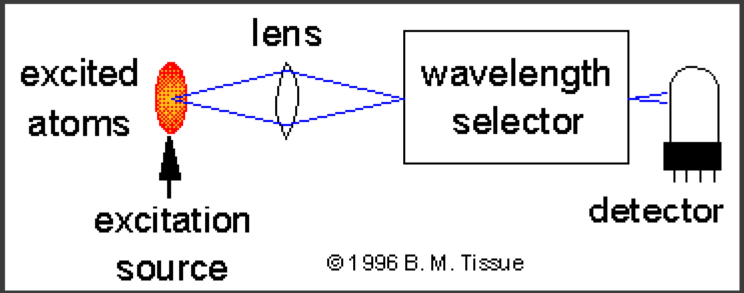


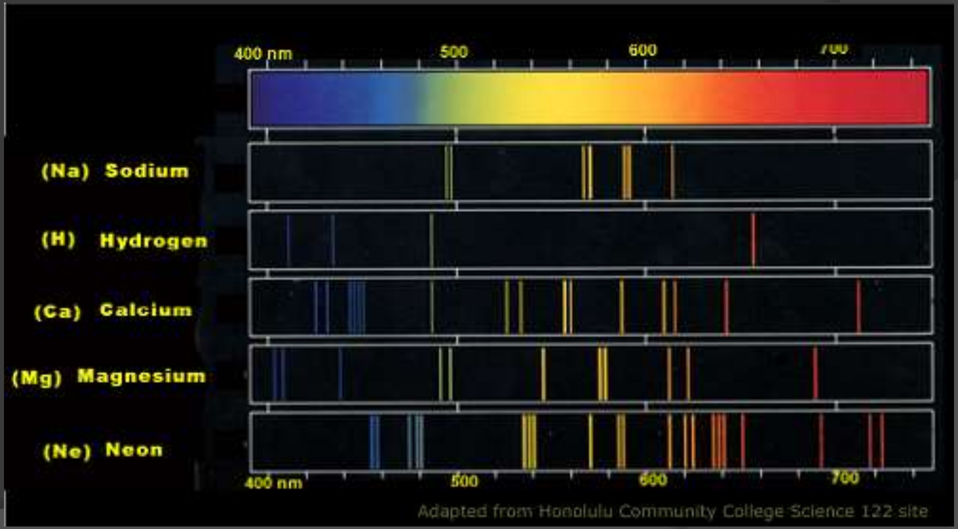




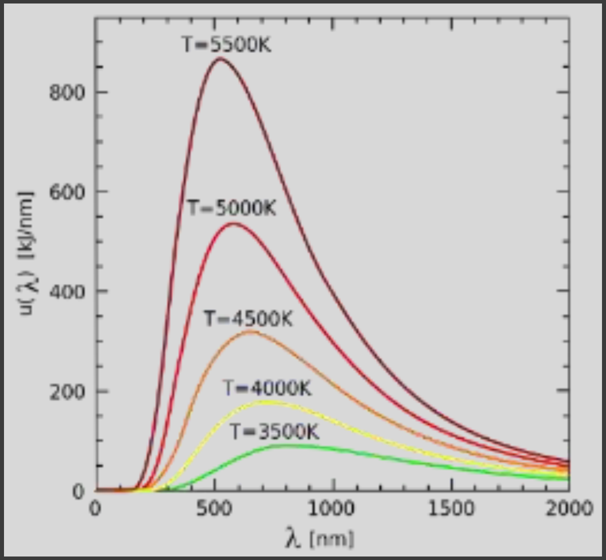
Spektroskopie 19-tého století







Gustav Kirchhoff (1824 – 1887)



Detektory 19-tého století

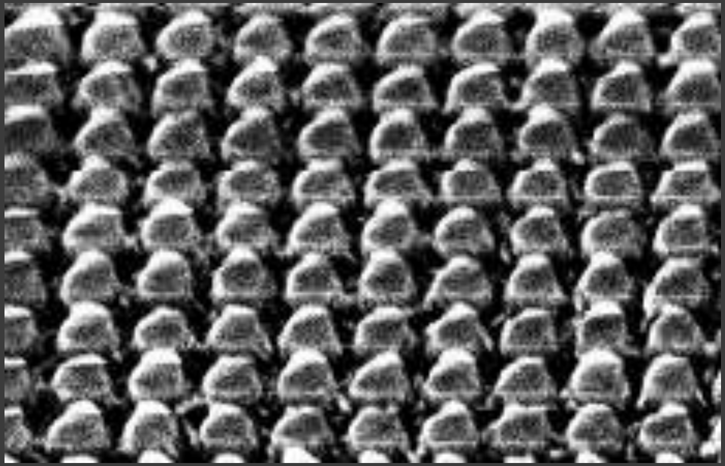
- oko
- teploměr
- fotografická deska

Problémy v IČ

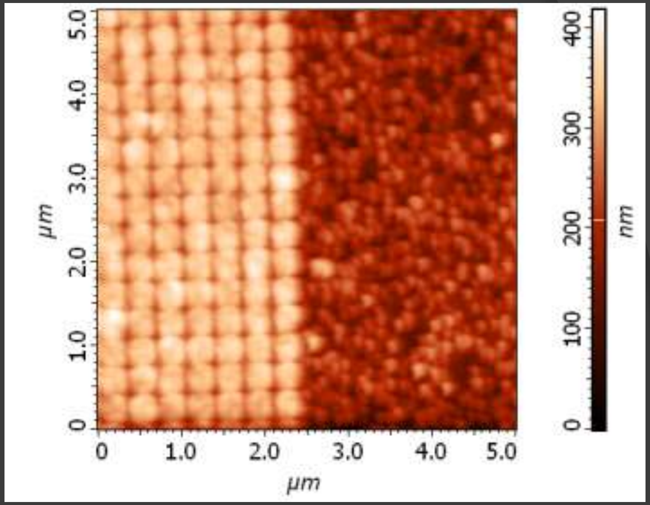
1. Zdroje nízke intenzity
2. Nízka citlivost detektorů
3. H_2O, CO_2

1. Horké těleso vytváří světlo se spojitým spektrem. Kirchhoff zavedl termín záření černého tělesa.
2. Plasma produkuje světlo se spektrálními čarami na diskrétních vlnových délkách, které závisí na druhu atomů v plynu. (emisní spektrum)
3. Horké těleso, obklopené chladnějším plynem, vytváří světlo s téměř kontinuálním spektrem, které má temné čáry při specifických vlnových délkách v závislosti druhu atomů v plynu. (absorpční spektrum)

Šíření světla v periodických strukturách
Fotonické krystaly



SEM image at angle: 45°: nano-pillars
ϕ=220 nm, gap 100 nm

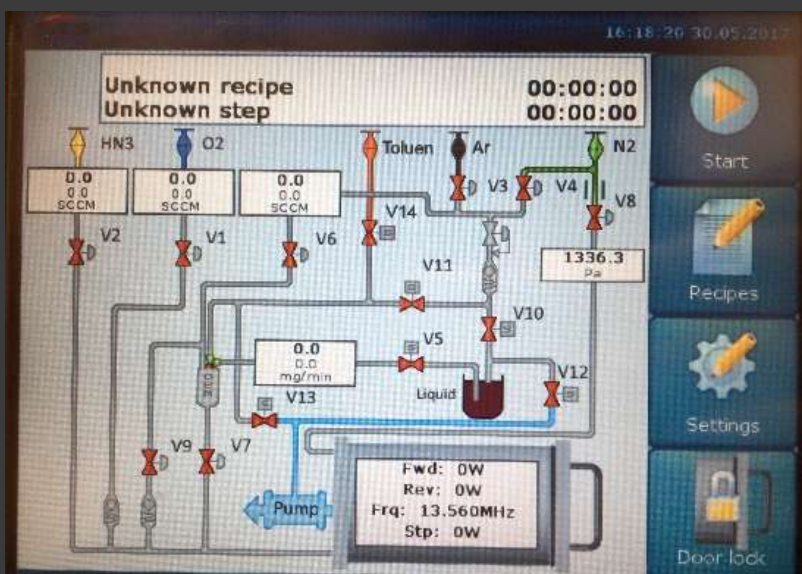


AFM image: nano-pillars height 140 nm

Ondic et al., *Effective Extraction of Photoluminescence from a Diamond Layer with a Photonic Crystal*, ACS Nano, 2011, 5 (1), pp 346–350

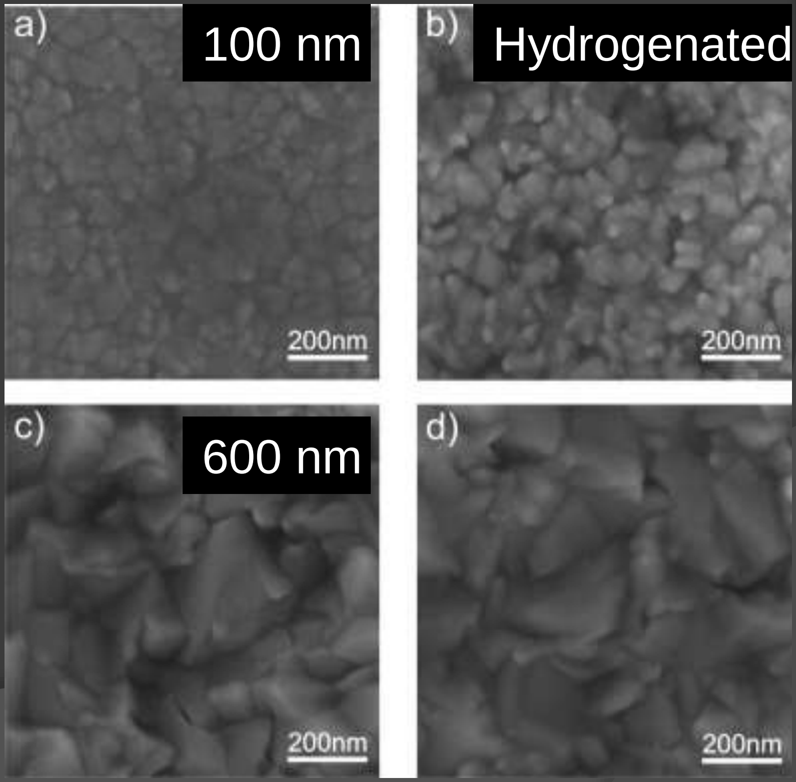
Inductively Coupled Plasma (ICP)

- 13.56 MHz, 300W
- Controlled evaporation & mixing
- Process gasses: N_2, Ar, O_2, NH_3
- „liquid droplets“
- Heated substrate
- Rotating cylinder for powder samples

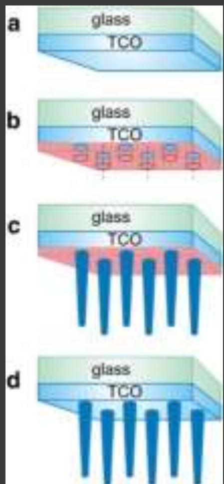


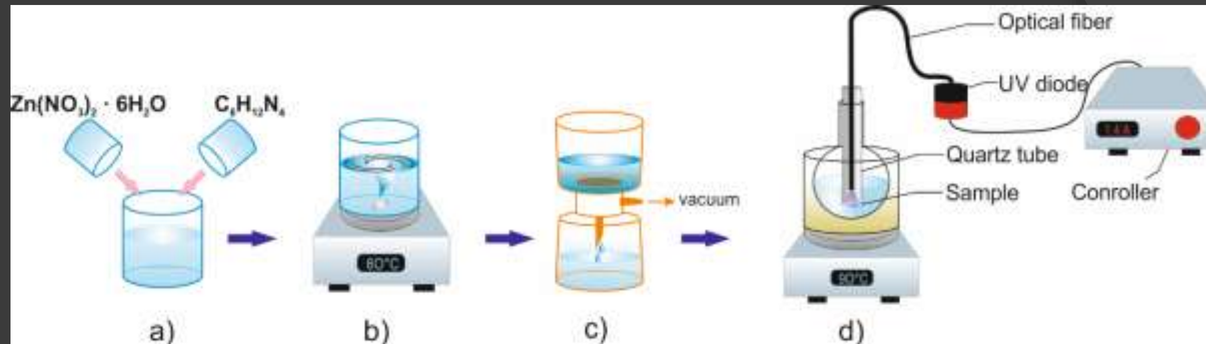
DC Magnetron Sputtering

- Background pressure 1mPa
- Plasma pressure   1 Pa
- Heated Cu stage up to 400°C
- Ar purity (99,999%), flow rate 2 sccm
- Target 400-500V, 0.14 A
- **Reactive sputtering of Zn** in Ar/O2 plasma
  - the reactive mixture of Ar and O2 (purity 99.95%)
  - flow rate 2.0 and 0.5 sccm
  - Intrinsic (resitive) layer
- **Sputtering of ZnO:Al target**
  - Typ. growth rate 20 nm/min
  - doped (conductive) layer



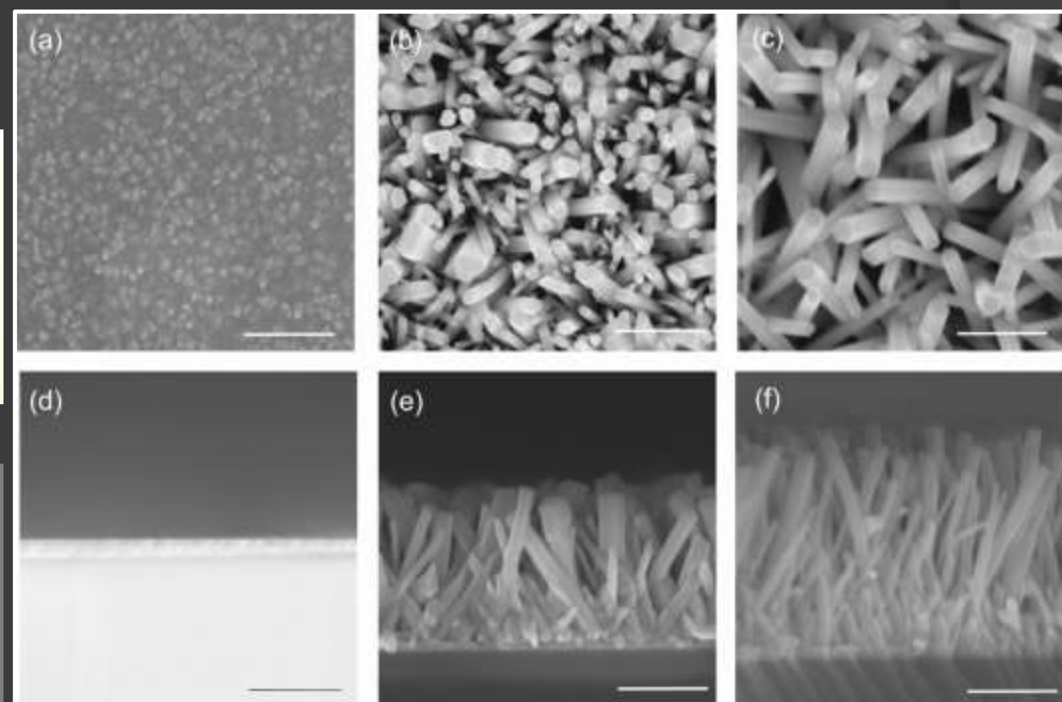
hydrothermal grow: hexamethylenetetramine (HMTA) + zinc nitrate hexahydrat :





Schematic drawing of the processing steps for preparation of the nutrient solution including mixing (a), heating and stirring (b) and supplementary filtration (c), and further growth of ZnO nanorods without and with UV irradiation (d).

- low temperature process (T<100 °C)
- simple equipment
- catalyst-free growth
- low cost
- deposition up to 7 x 7 mm^2
- environmental friendly & less hazardous



Scanning electron micrographs of ZnO sputtered seeding layer in top view (a) and cross section view (d) and ZnO NR's grown with (b,e) and without UV irradiation (c,f) in top and cross section view. Scale: 500 nm

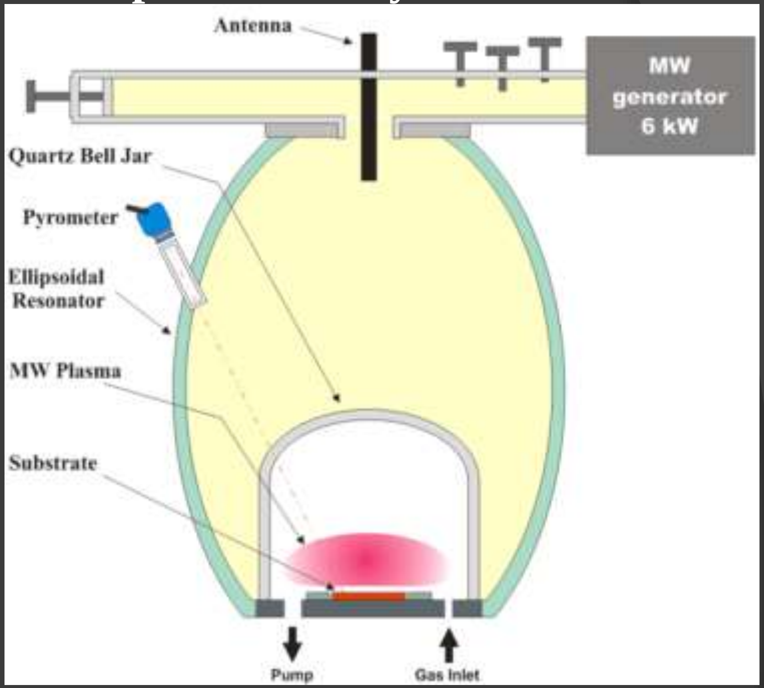
1] N. Neykova, J. Stuchlik, K. Hruska, A. Poruba, Z. Remes and O. Pop-Georgievski, *Study of the surface properties of ZnO nanocolumns used for thin-film solar cells,* Beilstein J. Nanotechnol. 2017, 8, 446–451. doi:10.3762/bjnano.8.48

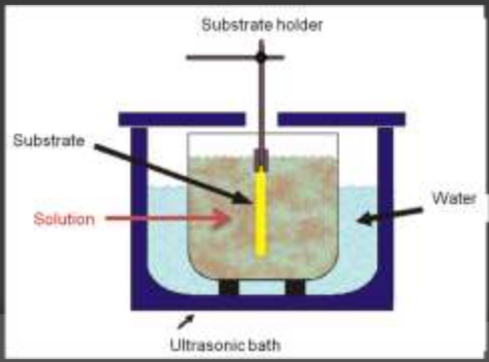
2] N. Neykova, Y.-Y. Chang, M. Buryi, M. Davydova, R. Kucerkova, D. Simek, Z. Remes, O. Pop-Georgievski, *Study of ZnO nanorods grown under UV irradiation,* Applied Surface Science, submitted

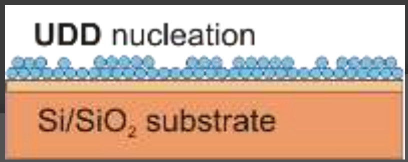
Diamond growth: Alex Kromka

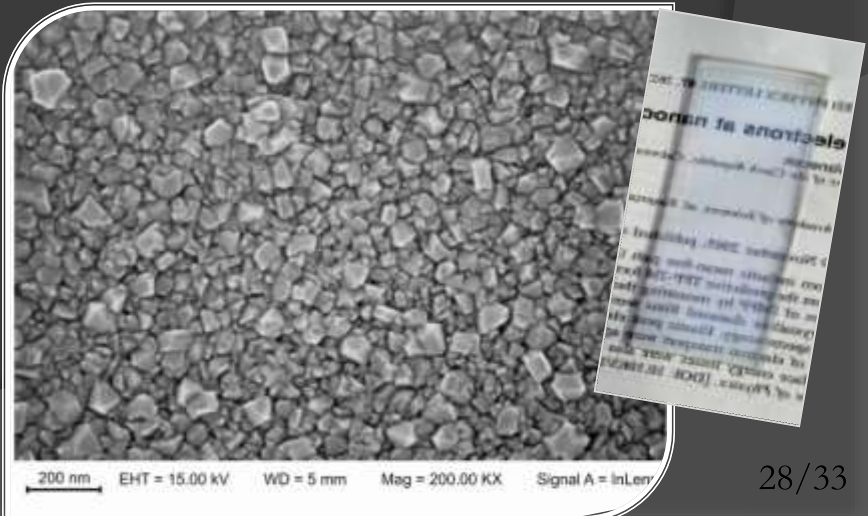
Focused MWCVD plasma reactor

Ellipsoidal cavity resonator

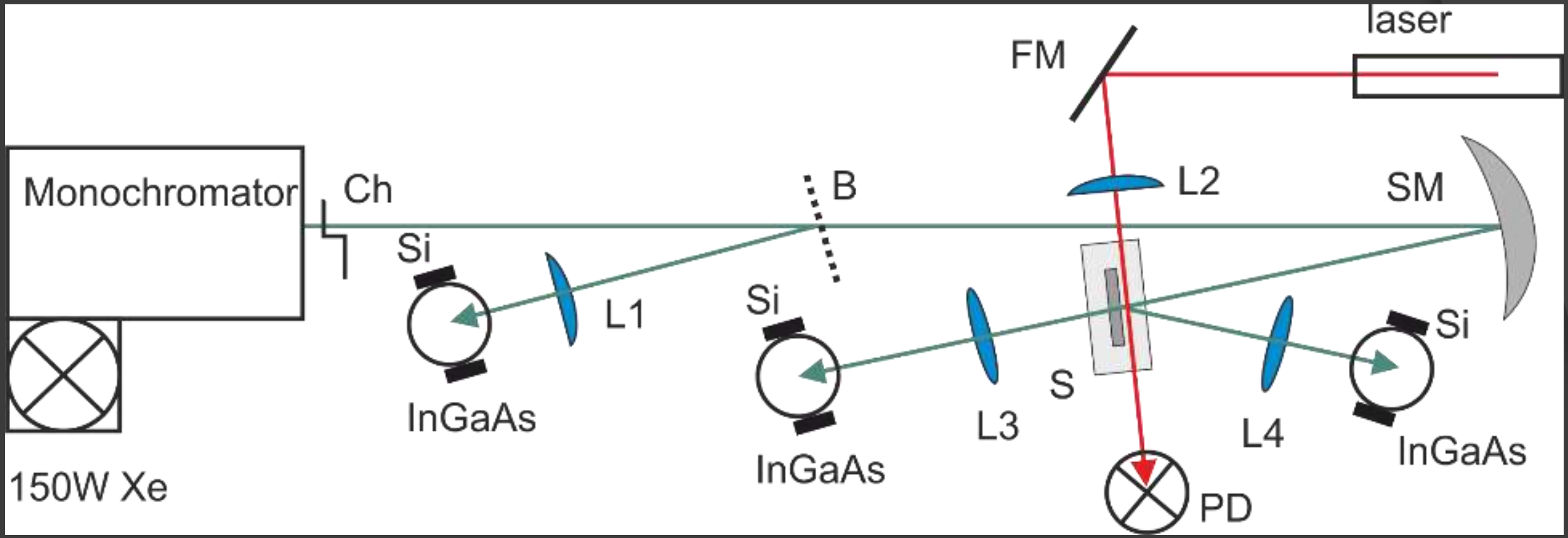


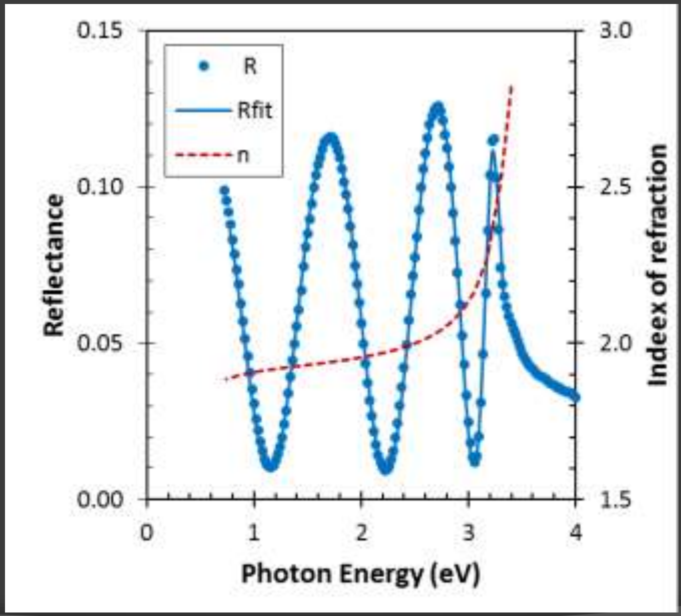


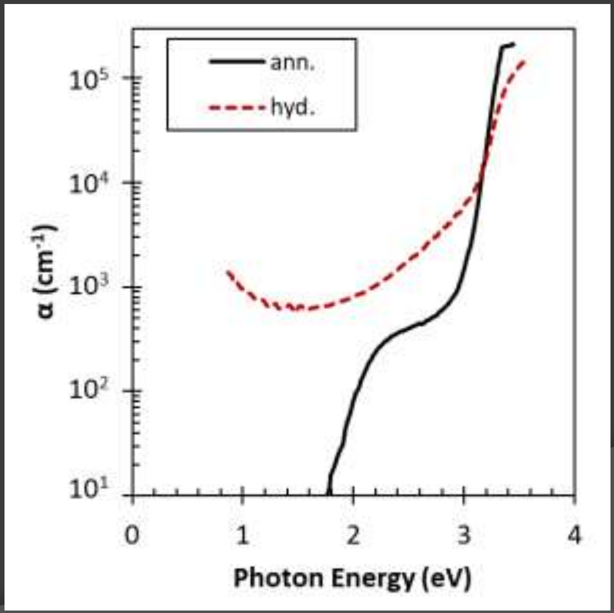


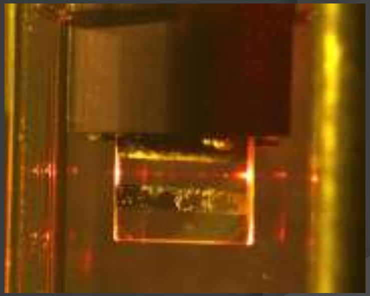


Optical absorption spectroscopy



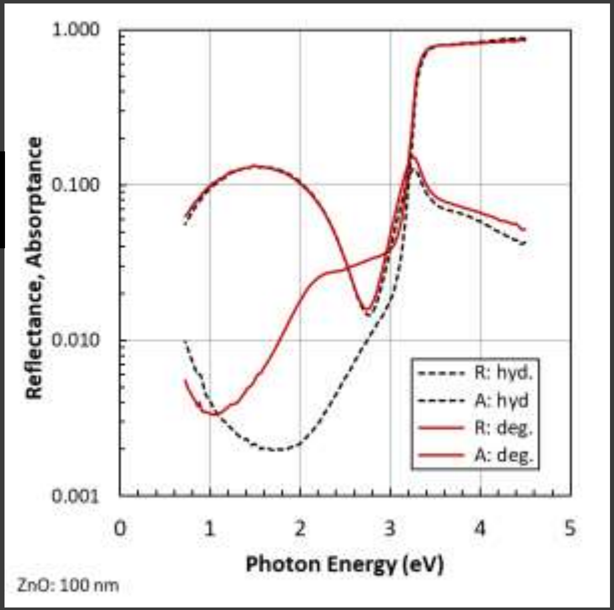


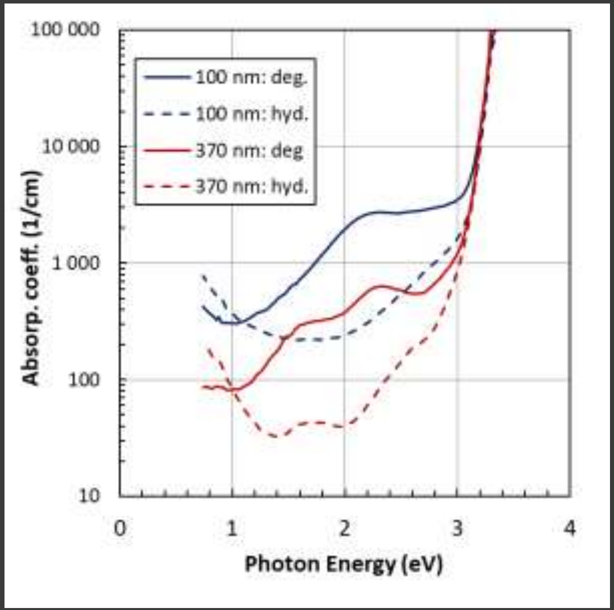


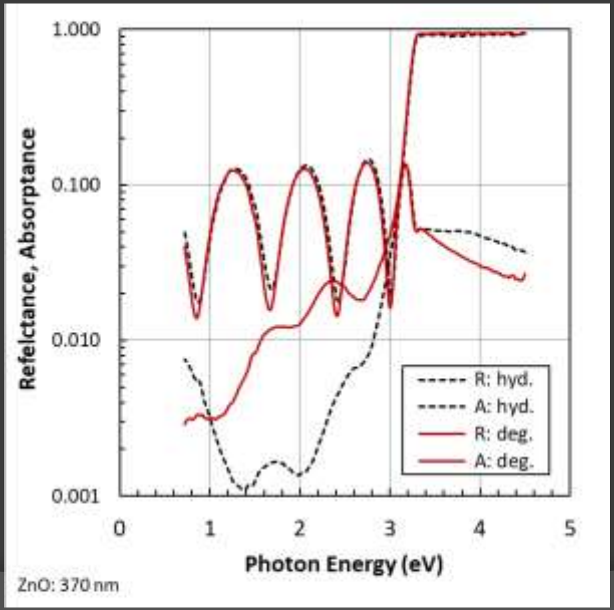


DC current hydrogenated ZnO thin film degradation

PDS
80
mA

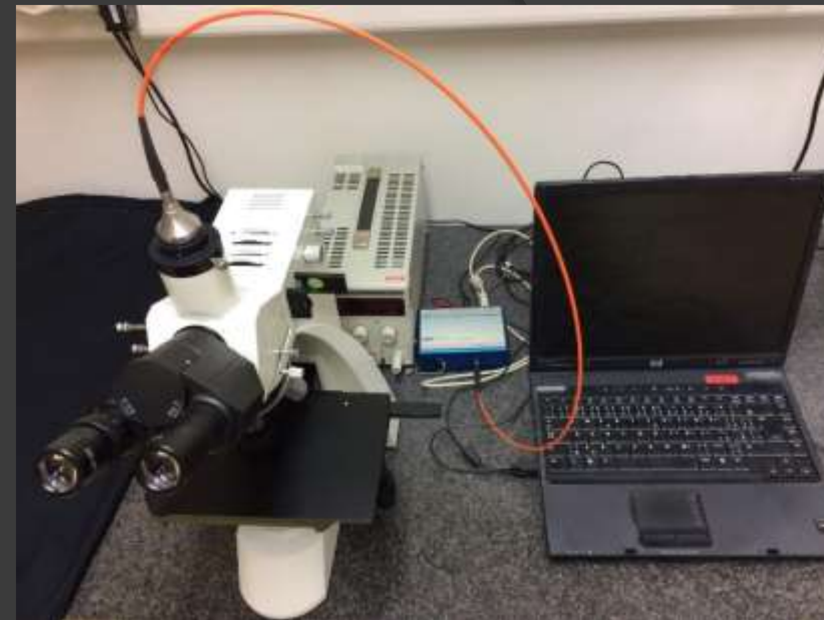




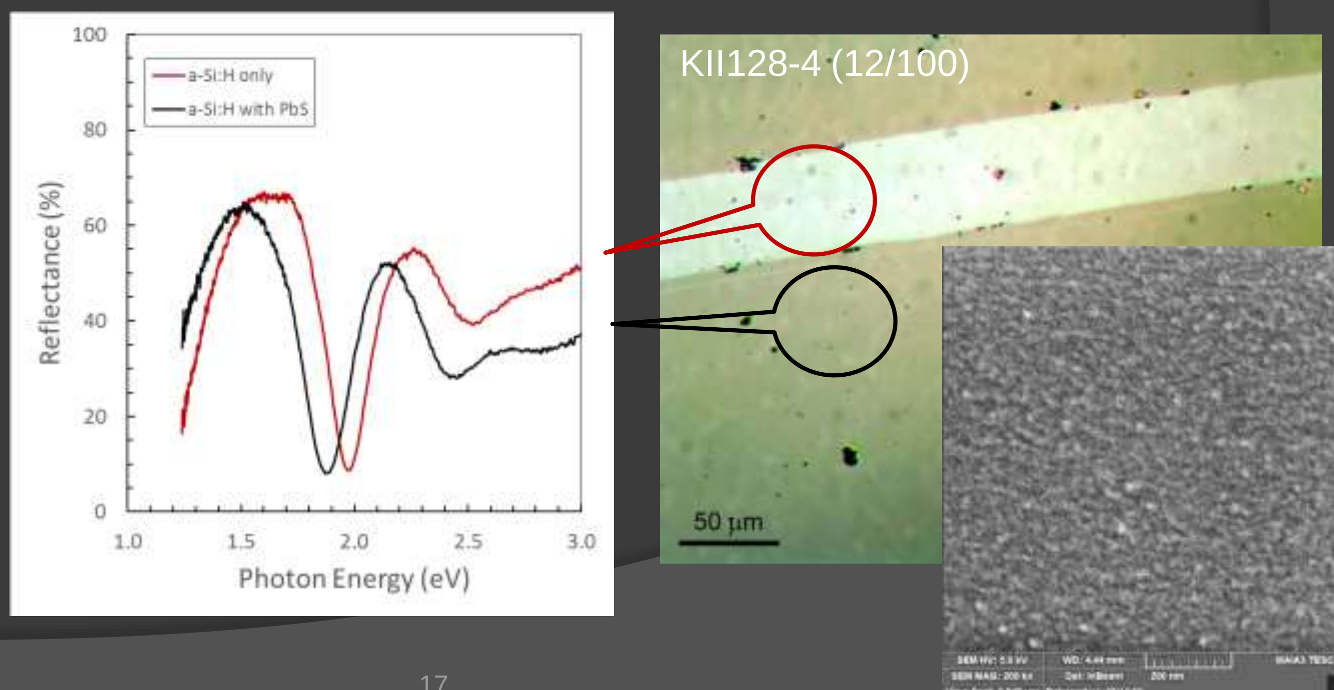


- Higher free electron conc. after hydrog
  => more efficient H diffusion in thin film
- No thin film thickness changes after degradation
- Optical absorp. edge at 3.3 eV (UV band gap @ 370
- Deep defects conc. increased after degradation
  -dominant defect at 2.3 eV (green @ 540 nm)
- Free electron conc. decreased after degradation
  => degradation of electronic properties
  => increase of the electrical resistivity

Reflectance of TF

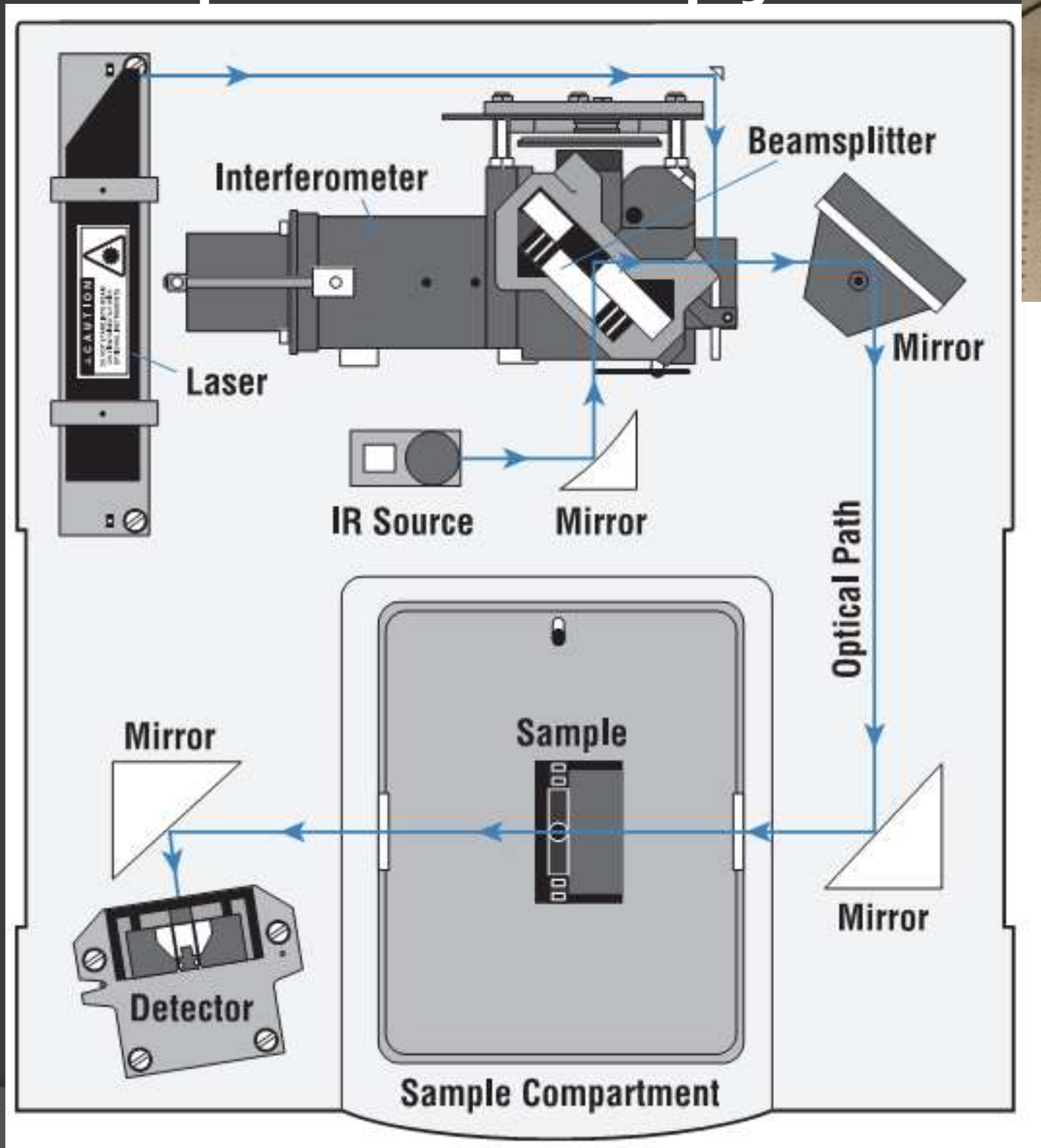


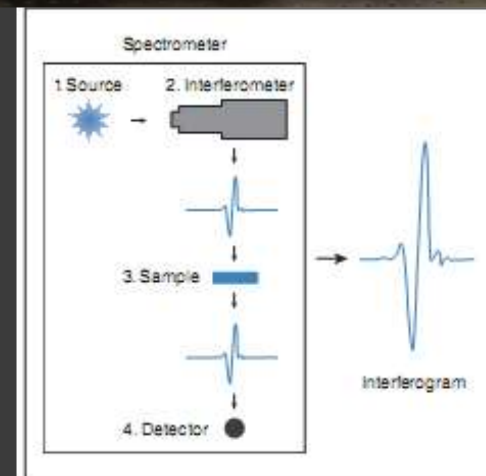
1. μ-Reflectance spectra 400−1000nm measured in optical microscope (20x)
2. 150 nm a-Si:H
3. Interference fringes phase change

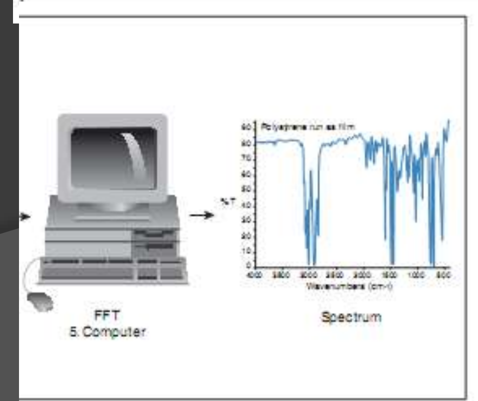


PbS thickness ~ 35 nm

IR spectroscopy





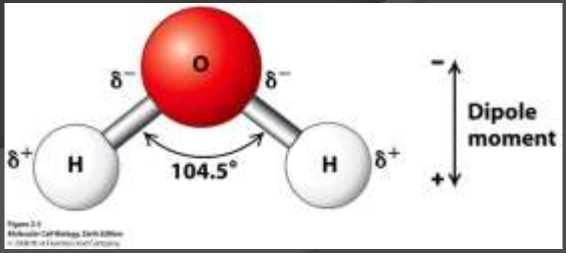


Basic rule of IR absorption

- Vibrations = stretching and bending movements of atoms in the molecules relative to each other by varying bond lengths (stretching) or bond angle (bending)
- Infrared absorption = The interactions of IR with matter may be changing molecular dipoles associated with vibrations and rotations.
- The electric dipole moment of the molecule must change during the vibration to absorb IR light

➢ IR Non-absorbing: O_2, H_2, N_2, Si, C

➢ IR Absorbing: H_2O, CO_2, CH_4



Molecular vibration examples

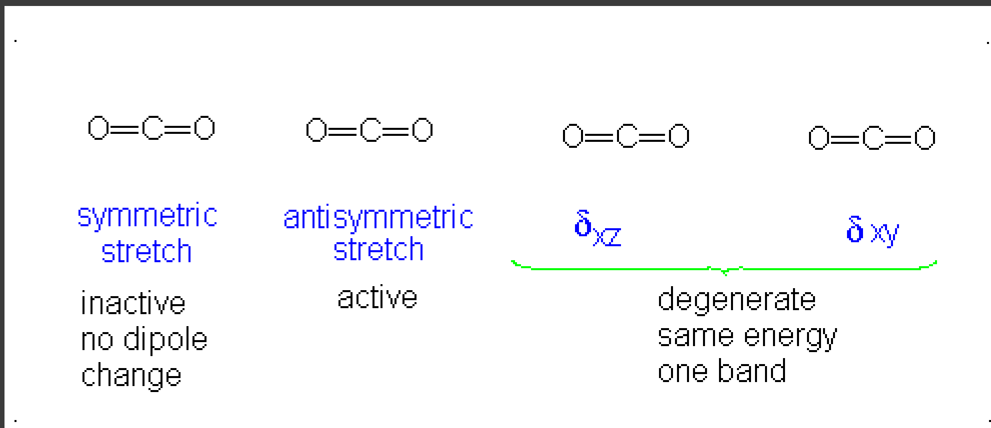
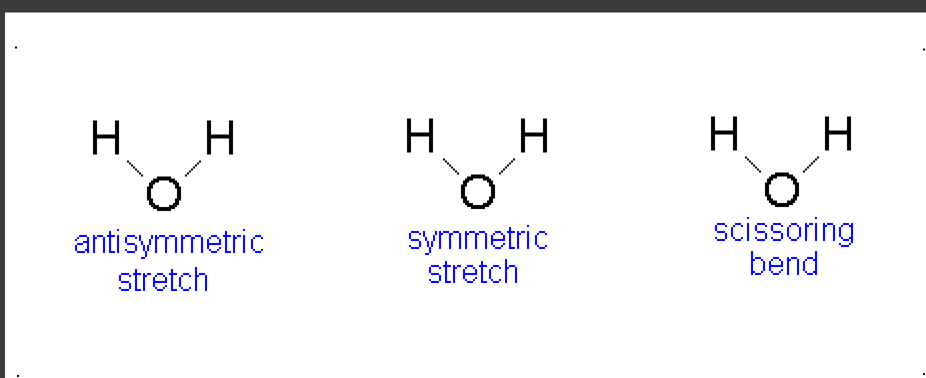


Table 1.1 Degrees of freedom for polyatomic molecules. From Stuart, B., *Modern Infrared Spectroscopy*, ACOL Series, Wiley, Chichester, UK, 1996. © University of Greenwich, and reproduced by permission of the University of Greenwich

Type of degrees of freedom	Linear	Non-linear
Translational	3	3
Rotational	2	3
Vibrational	$3N-5$	$3N-6$
Total	$3N$	$3N$

degrees of freedom 3*N-5 = 3*3-5 = 4



1. The Symmetric Stretch at 3685 cm^{-1}
2. The Asymmetric Stretch at 3506 cm^{-1})
3. Bend at 1885 cm^{-1}

degrees of freedom 3*N-6 = 3*3-6 = 3

Applications of the Infrared spectroscopy

- Commercial accessories for solid, liquid and gas samples
- Existing spectra databases
- Analysis of fuel and lubricants, polymers, proteins, gases
- kinetics of chemical reactions (ms resolution)
- study of phonons, defects, donors and acceptors
- Our applications: **Qualitative analysis of functionalized surfaces and functionalized nanoparticles**

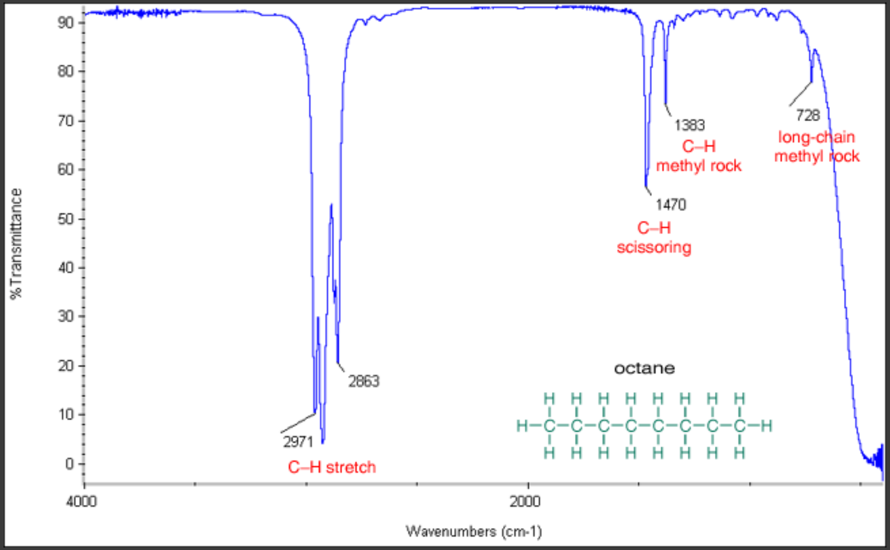
Approach to modelling of vibrations of functional groups

- take care when using IR data tables or data for isolated molecules for interpreting spectra of funcionalized surfaces

- The shift of the functional group vibrations to higher frequencies with the surface coverage (Dynamic Dipole Effect)

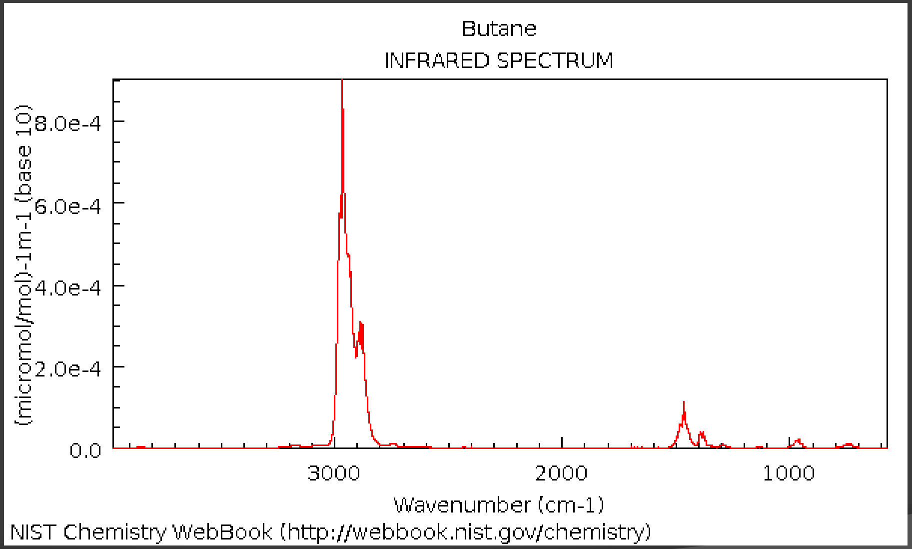
- the effect of surface orientation and morphology

- more experimental information (XPS, HRTEM, chemical treatment,) is needed to guess structures



Transmission spectrum

$$T = \frac{S}{B}$$



Absorbance spectrum

$$A = -\ln\frac{S}{B}$$

ATR & GAR FTIR

Applied Surface Science 270 (2013) 411–417

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Diamond-coated ATR prism for infrared absorption spectroscopy of surface-modified diamond nanoparticles

Z. Remes[a,*], H. Kozak[a], B. Rezek[a], E. Ukraintsev[a], O. Babchenko[a], A. Kromka[a], H.A. Girard[b], J.-C. Arnault[b], P. Bergonzo[b]

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Nanopowder

ABSTRACT

Linear antenna microwave chemical vapor deposition process was used to homogeneously coat a 7 cm long silicon prism by 85 nm thin nanocrystalline diamond (NCD) layer. To show the advantages of the NCD-coated prism for attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) of nanoparticles, we apply diamond nanoparticles (DNPs) of 5 nm nominal size with various surface modifications by a drop-casting of their methanol dispersions. ATR-FTIR spectra of as-received, air-annealed, plasma-oxidized, and plasma-hydrogenated DNPs were measured in the 4000–1500 cm^{-1} spectral range. The spectra show high spectral resolution, high sensitivity to specific DNP surface moieties, and repeatability. The NCD coating provides mechanical protection against scratching and chemical stability of the surface. Moreover, unlike on bare Si surface, NCD hydrophilic properties enable optically homogeneous coverage by DNPs with some aggregation on submicron scale as evidenced by scanning electron microscopy and atomic force microscopy. Compared to transmission FTIR regime with KBr pellets, direct and uniform deposition of DNPs on NCD-ATR prism significantly simplifies and speeds up the analysis (from days to minutes). We discuss prospects for in situ monitoring of surface modifications and molecular grafting.

Diamond & Related Materials 20 (2011) 882–885

Contents lists available at ScienceDirect

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journal homepage: www.elsevier.com/locate/diamond

Grazing angle reflectance spectroscopy of organic monolayers on nanocrystalline diamond films☆

Z. Remes *, H. Kozak, O. Babchenko, S. Potocky, E. Ukraintsev, B. Rezek, A. Kromka

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Keywords:
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Infrared spectroscopy
Functionalization
Grazing angle
Brewster angle

ABSTRACT

The nanocrystalline diamond (NCD) layers were grown by the large area (linear plasma) MWCVD on polished silicon substrates with and without intermediate mirror-like metallic coatings. The optical reflectance and Raman spectroscopy in the ultraviolet, visible and near infrared region (UV–VIS–NIR) reveals the thickness and the optical quality of NCD layers. The modified grazing angle reflectance (GAR) spectroscopy is applied in the mid infrared region 800–4000 /cm to detect the molecular vibrations (functional groups) at the functionalized NCD surface. The optical absorbance of functionalized NCD surface is evaluated from p-polarized reflectance spectra measured at Brewster angle of incidence (BAR) to eliminate the interference fringes. We report a significant enhancement of sensitivity of BAR using NCD growth on metal mirrors.

Langmuir

Article

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Nanostructured Diamond Layers Enhance the Infrared Spectroscopy of Biomolecules

Halyna Kozak,* Oleg Babchenko, Anna Artemenko, Egor Ukraintsev, Zdenek Remes, Bohuslav Rezek, and Alexander Kromka

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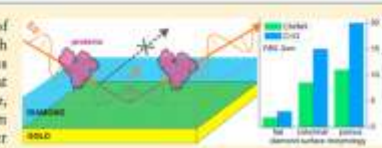
ABSTRACT: We report on the fabrication and practical use of high-quality optical elements based on Au mirrors coated with diamond layers with flat, nanocolumnar, and nanoporous morphologies. Diamond layers (100 nm thickness) are grown at low temperatures (about 300 °C) from a methane, carbon dioxide, and hydrogen gas mixture by a pulsed microwave plasma system with linear antennas. Using grazing angle reflectance (GAR) Fourier transform infrared spectroscopy with p-polarized light, we compare the IR spectra of fetal bovine serum proteins adsorbed on diamond layers with oxidized (hydrophilic) surfaces. We show that the nanoporous diamond layers provide IR spectra with a signal gain of about 600% and a significantly improved sensitivity limit. This is attributed to its enhanced internal surface area. The improved sensitivity enabled us to distinguish weak infrared absorption peaks of <10-nm-thick protein layers and thereby to analyze the intimate diamond–molecule interface.



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