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Winter College on Optics: Fundamentals of Photonics - Theory, Devices and Applications

10 - 21 February 2014

Photonic materials and measurement techniques

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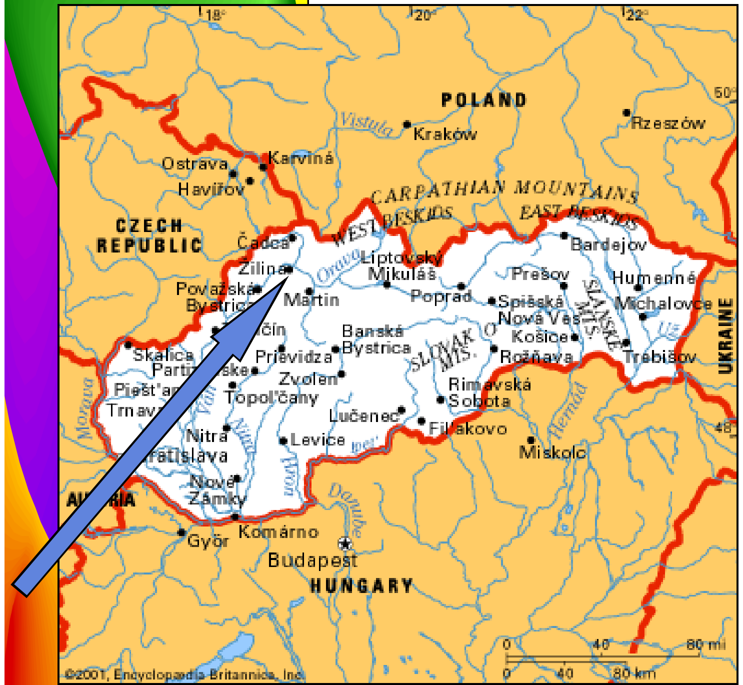
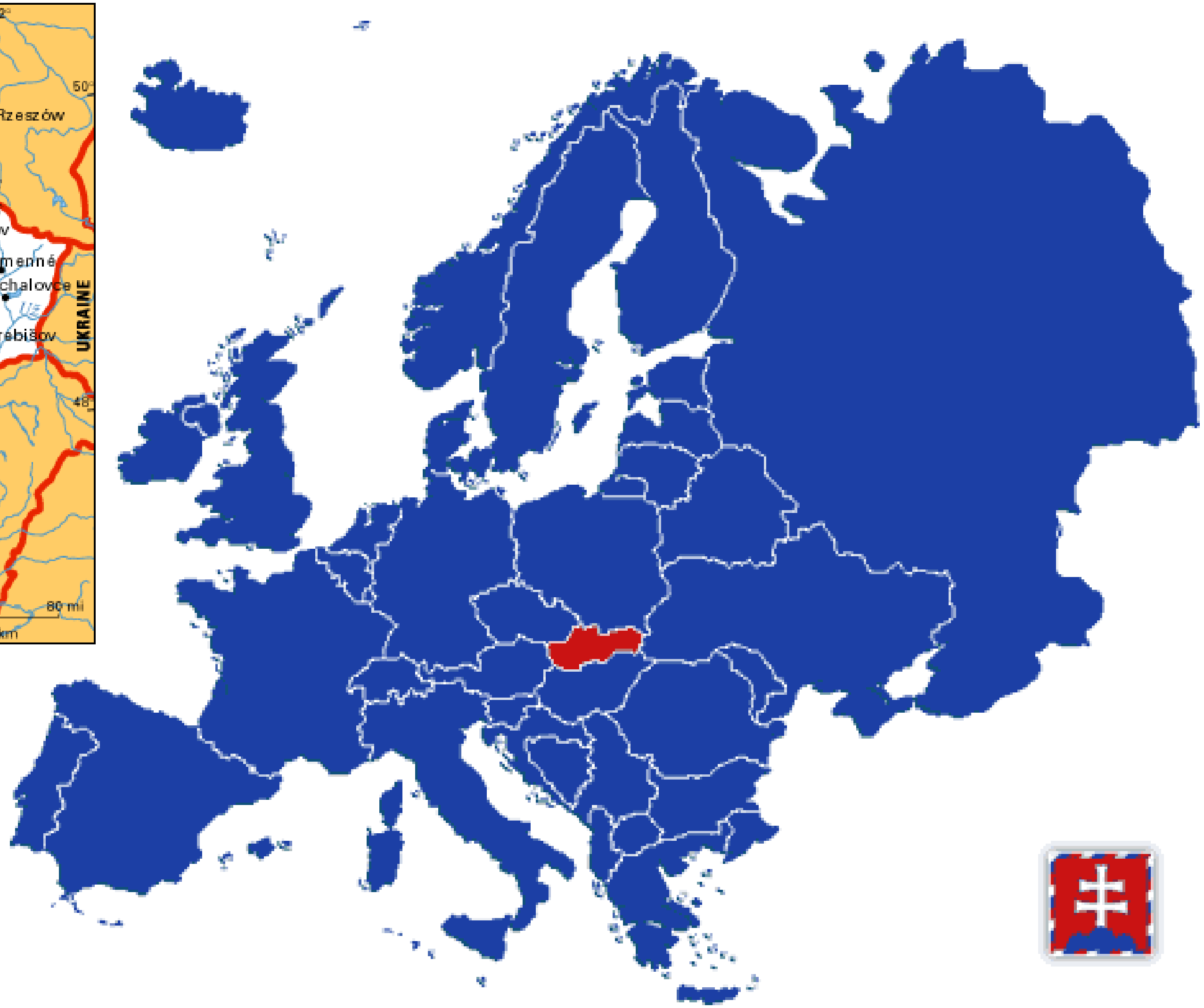
ICTP: Winter College of Optics
Trieste February 2014

University of Žilina, Slovakia





History

More than 63 000 graduates - 9700 at Fculty of El. Eng.

1st October 1953 — **Railway College**

- Faculty of Electrical Engineering
- Faculty of Mechanical Engineering
- Faculty of Civil Engineering
- Faculty of Transport
- Military Faculty

Prague, Czech Republic

1959 — **University of Transport Prague**

1960-62 — **University of Transport Žilina**

1978 — **University of Transport and Communications Žilina**

1989

1996 — **University of Žilina**

ŽU: 11 500 students
650 university teachers
1 500 employees

ACERT ISO 9001

1953 - 2013

ŽILINSKÁ UNIVERZITA
V ŽILINE

University of Žilina

www.uniza.sk

provides a full range of technological, economic, management, and a limited range of humanistic and natural science education at under-graduate, graduate and post-graduate levels

7 faculties and other institutes

Faculty of Operation and Economics of Transport and Communications
Faculty of Mechanical Engineering
Faculty of Electrical Engineering
Faculty of Civil Engineering
Faculty of Management Science and Informatics
Faculty of Special Engineering
Faculty of Humanities

Faculty of Electrical Engineering

- founded in 1953 as one of the basic faculties of the Railway College in Prague,
- re-established in 1992

At present:

- 8 departments including the Institute of Aurel Stodola in Liptovský Mikuláš
- 1600 students

traditional educational activities - completed by new branches, which are typical for research and technological development:

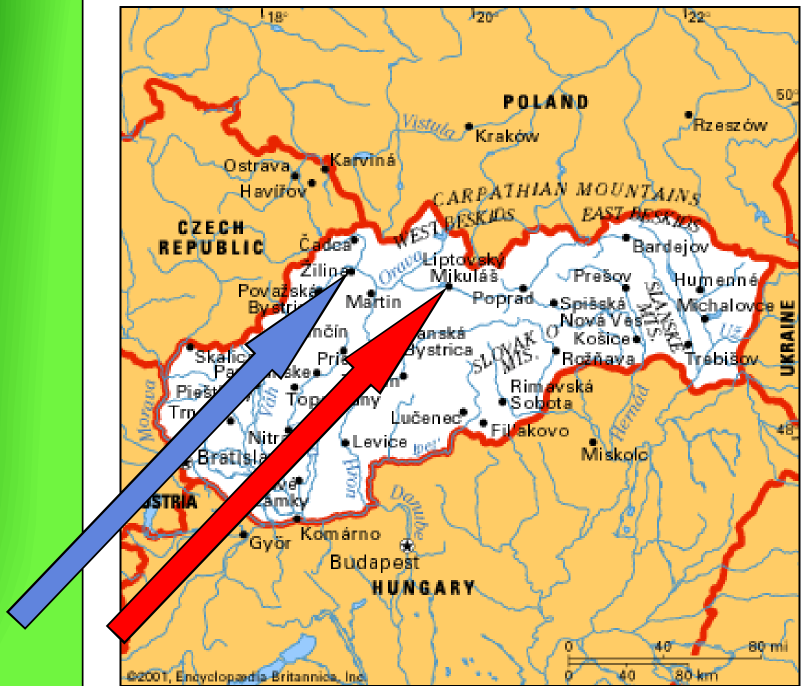
- information technologies
- power electronic systems
- telecommunications
- modern methods for control of electric networks
- study of interdisciplinary branches, like mechatronics and biomedicine

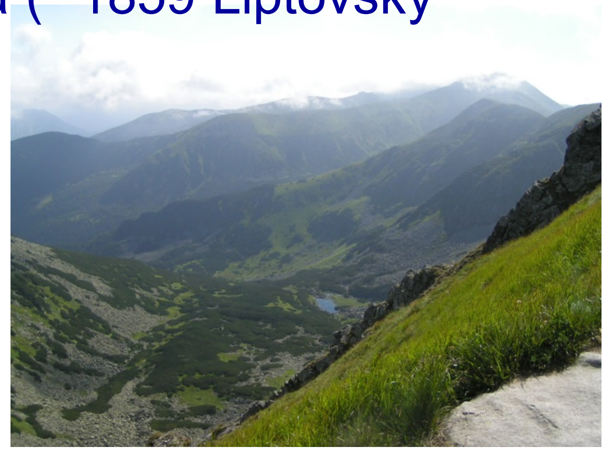
www.fel.uniza.sk

Institute of Aurel Stodola

www.lm.uniza.sk

- Institute of Aurel Stodola of the Faculty of Electrical Engineering, University of Žilina
- Founded in 2002, since 2012 named after a great researcher and inventor Aurel Stodola (* 1859 Liptovský Mikuláš, † 1942 Zürich)





Outline

1. **Introduction**
2. **Motivation**
3. **Thin films**
4. **Measurement techniques**
5. **Photonics materials**

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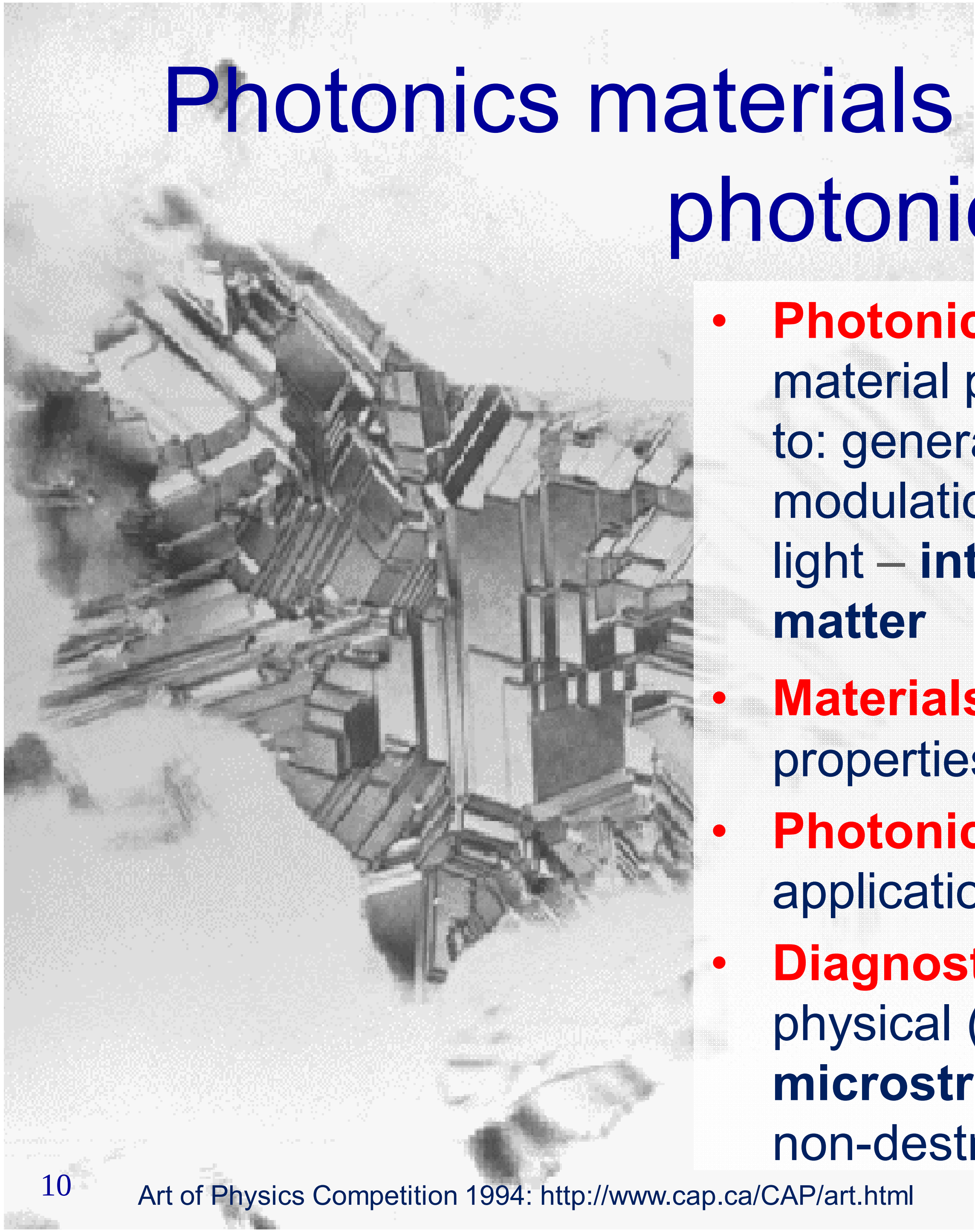
Motivation

“There is:

- **no science without measurements**,
- **no quality without testing**,
- no global markets without standards”.

Commission of the European Union

Photonics materials = materials for photonics

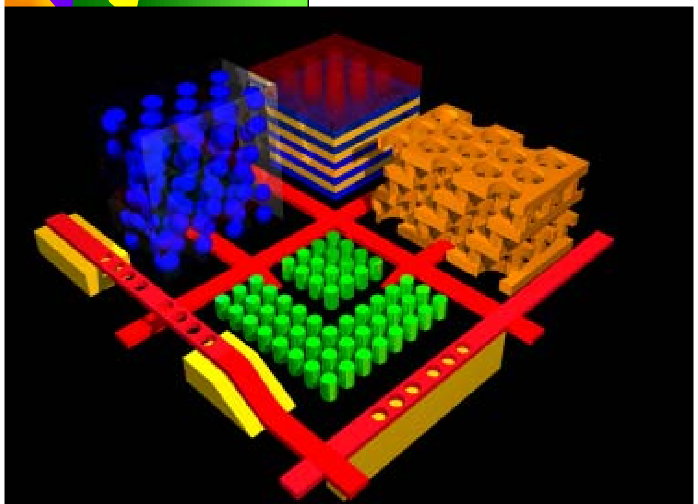


- **Photonics** – manipulation of light by material particles (electrons) leading to: generation, propagation, modulation, amplification, detection of light – **interaction of light and matter**
- **Materials** – new and often exotic ☺ properties and their engineering
- **Photonics** – wide area of applications
- **Diagnostics** – determination of physical (optical) properties, esp. **microstructure** using feasible and non-destructive measurements

Art of Physics Competition 1994: http://www.cap.ca/CAP/art.html

Photonics or photonic materials?

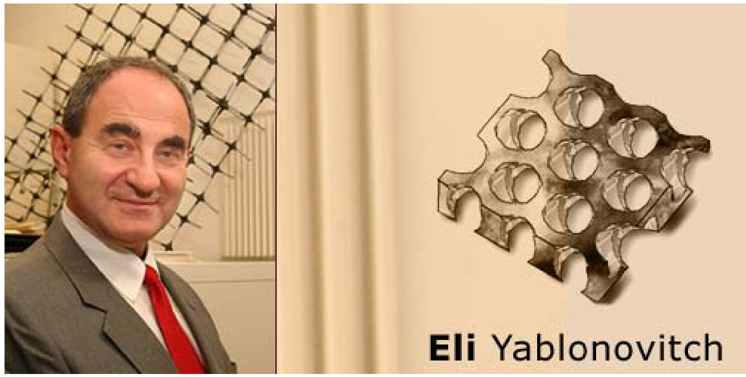
- **Photonics (optical) materials** – materials for manipulating light (photons) by material leading to a certain function: generation, propagation etc. of light – **interaction of light and matter**
- **Photonic materials** - **new attractive type of materials** displaying unusual properties when interacting with light – e.g. by dielectric periodicity (periodic refractive index) we can achieve **tailored dispersion relations and tailored stop bands** for light propagating through material, e.g.



localizing light in specific areas and

preventing light propagating in certain directions – photonic band gaps

J.D. Joannopoulos: Photonics Crystals: Molding the Flow of Loght, Princeton Univ. Press 2008



Idea first advanced by Eli Yablonovitch in 1987, Univ. of California, Berkeley, in 1990 he built the first photonic crystal

Photonics materials applications

Material research reflecting infinity

- **Telecommunications** – optical fiber comunications, free space optics, remote control …
- **Information processing** – data recording and reading, holography …
- **Power engineering** – photovoltaics …
- **Medicine & biology** – laser surgery, endoscopy, physiological and/or pathological diagnostics …
- **Industry** – machinery manufacturing (welding, cutting, drilling …)
- **Aviation, military** – sensors, remote control, navigation …
- **Entertainement** – laser shows, holography …

Art of Physics Competition 2012: http://www.cap.ca/CAP/art.html

Motivation

Research on photonics materials, components and systems:

- **Advanced material science** – materials of **novel physical properties** including properties engineering
- **Photonics materials**: a wide range of semiconductors (Si, Ge, III-V, organics …), glasses, new dielectrics (high-k materials), liquid crystals, organics, photonic crystals

Photonics materials:

- Composition - novel or standard

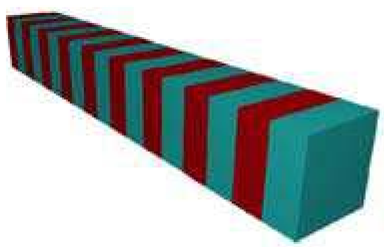
- Structure & microstructure – novel or standard

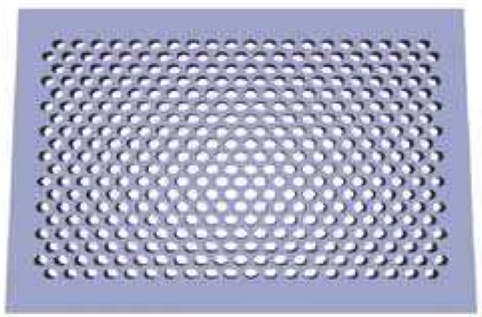
- Preparation technology – novel or standard

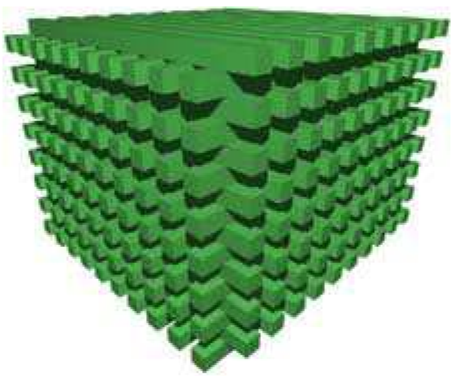
Diversity in dimensionality

Research on photonics materials, components and systems:

- bulk
- thin films, very thin films, ultra-thin films and thin films structures (1887 Lord Rayleigh experimented with multilayer dielectric stacks and showed that they had a 1D photonic band-gap)
- periodic structures
- subwavelength dimensions







A. Mock, L. Lu, In: Recent optical and photonic technologies, Ed. Ki Young Kim, INTECH, 2010

Outline

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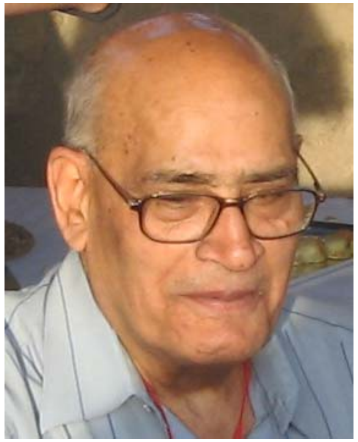
3. **Thin films**
4. Measurement techniques
5. Photonics materials

Thin film concepts



A thin film:

Optical definition- the thickness is in order of the wavelength of light

General definition – an object the physical properties of which differ from properties of the same material in bulk

The origin of the difference is microstructure connected with the deposition process!

Kasturi Lal Chopra:

... A thin film is a material created ab initio by the random nucleation and growth processes of individually condensing/reacting atomic/ionic /molecular species on a substrate.

… structural, chemical and physical properties are strongly dependent on a large number of deposition parameters and may also be thickness dependent.

…The nucleation and growth processes bestow new and exotic properties to thin-film materials that can be controlled and reproduced, provided a range of deposition parameters are monitored and controlled precisely.

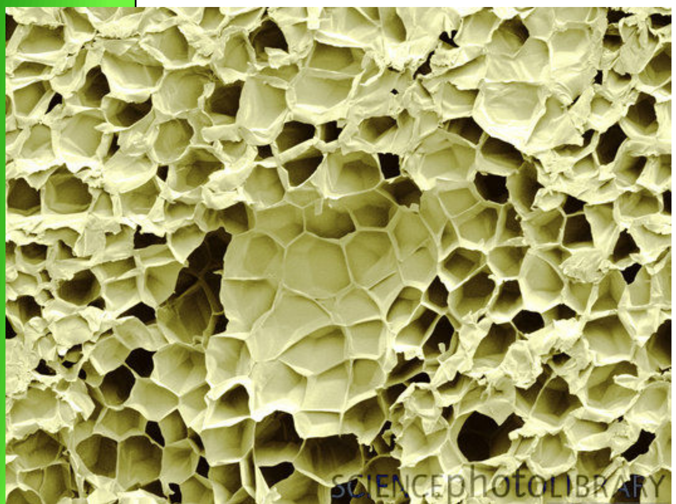
Chopra K.L.: Thin-Film Phenomena. McGraw-Hill: New York, 1969
Chopra K.L.: Thin Film Solar Cells, Plenum Press 1983

A thin film

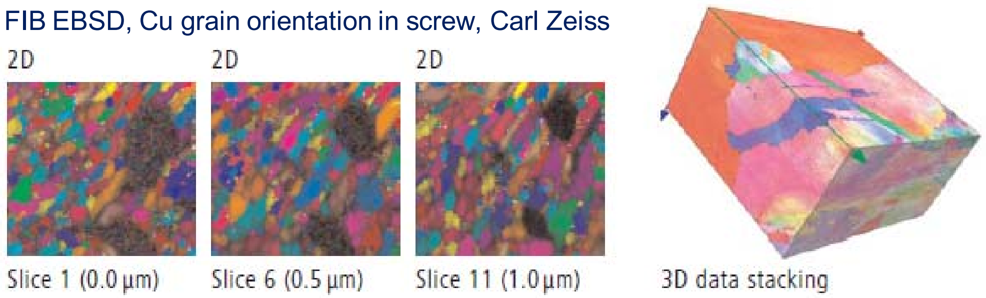
Microstructure

Microstructure … microscopic description and spatial distribution of material constituents, e.g. volume fractions of individual phases of multiphase material, crystalline grains, grain boundaries etc.

Microstructure investigation – common imaging and analytical methods of high spatial resolution=micro-beam instruments such as a TEM, SEM (potentially equipped with EDS), e-beam scatter diffraction (EBSD, FIB EBSD), electron-probe micro-analyser, X-Ray diffraction …

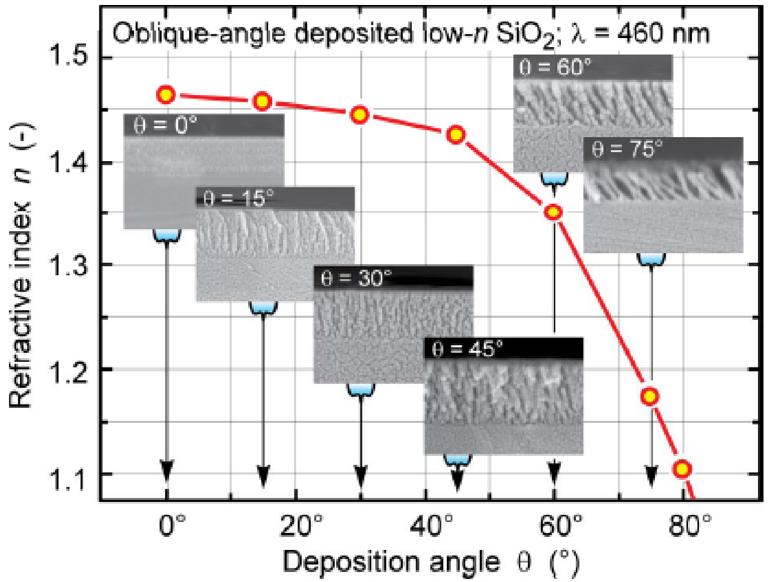


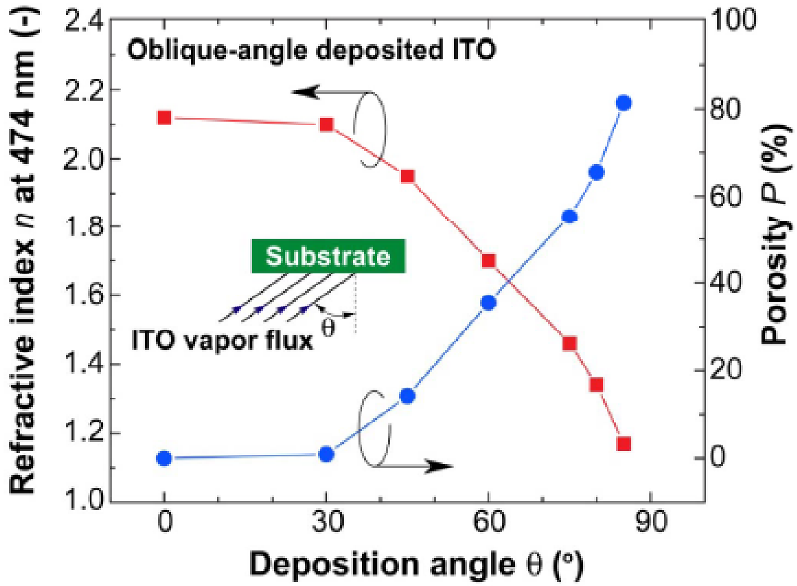
FIB EBSD, Cu grain orientation in screw, Carl Zeiss



SEM Popcorn microstructure, MAGN 180x

Playing with microstructure





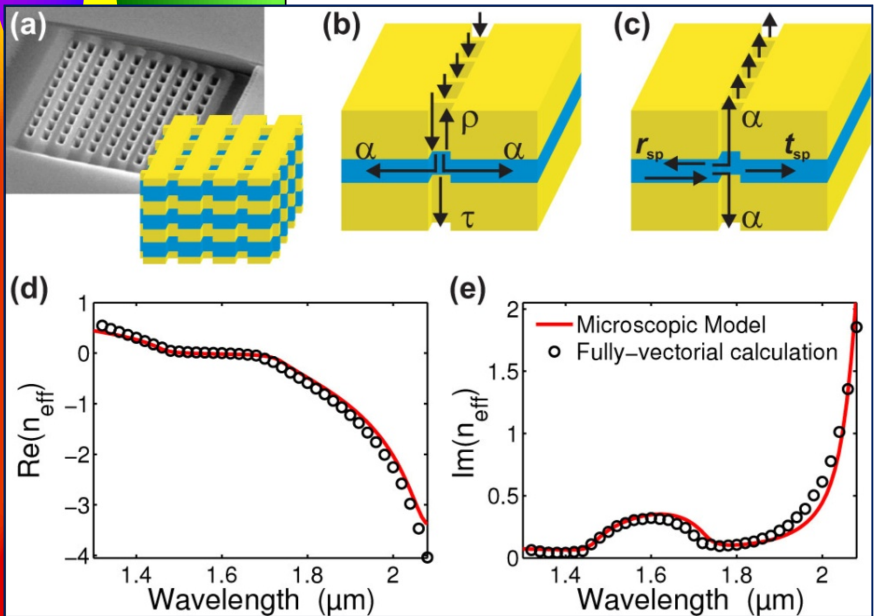
- ***Controllability*** of refractive index of a film by varying deposition angle
- $1.46 < n_{SiO2} <$ **1.05**; $2.19 < n_{ITO} < 1.17$
- Design freedom in optical components afforded by oblique angle deposition
- Select materials based on materials properties other than refractive index, and tune the refractive index to desired value

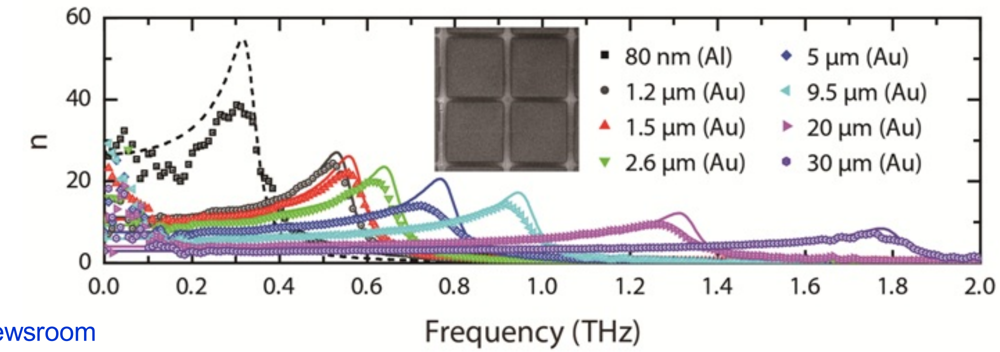
E.F. Schubert, J.K.Kim, 7th Intern. Conf. NUSOD, 2007

More design flexibility - metamaterials

- artificial media created by subwavelength structuring – controlling light propagation
- going beyond the limit attainable with naturally existing substances …
- a vast variety of unexpected physical phenomena …
- experimental realization of a negative refractive index … expanding the refractive index into a high positive regime
- provide more design flexibility for “transformation optics”

(*Bumki Min, the Korean Advanced Institute for Science and Technology*)

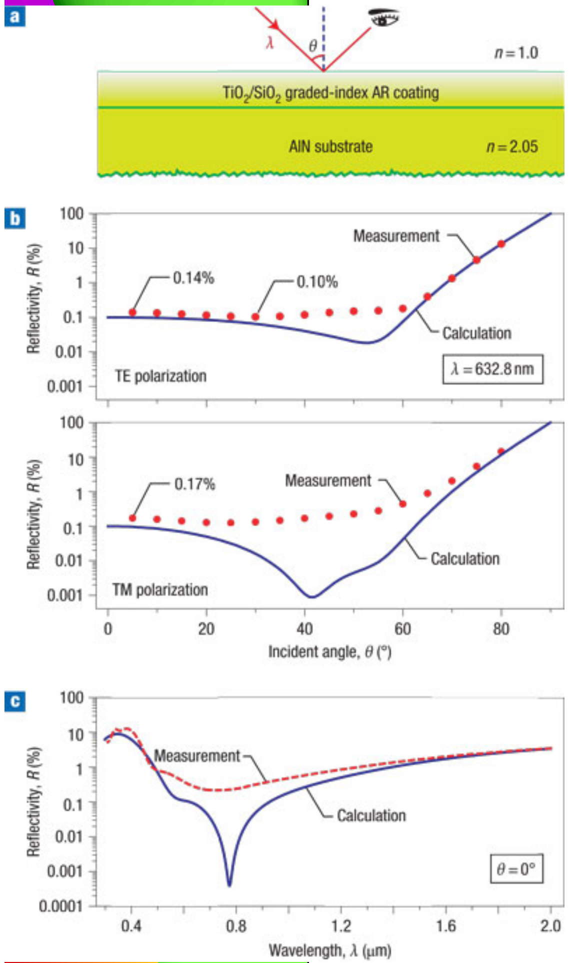




J.Yang, Ch. Sauvan and P. Lalanne: 26 May 2011, SPIE Newsroom

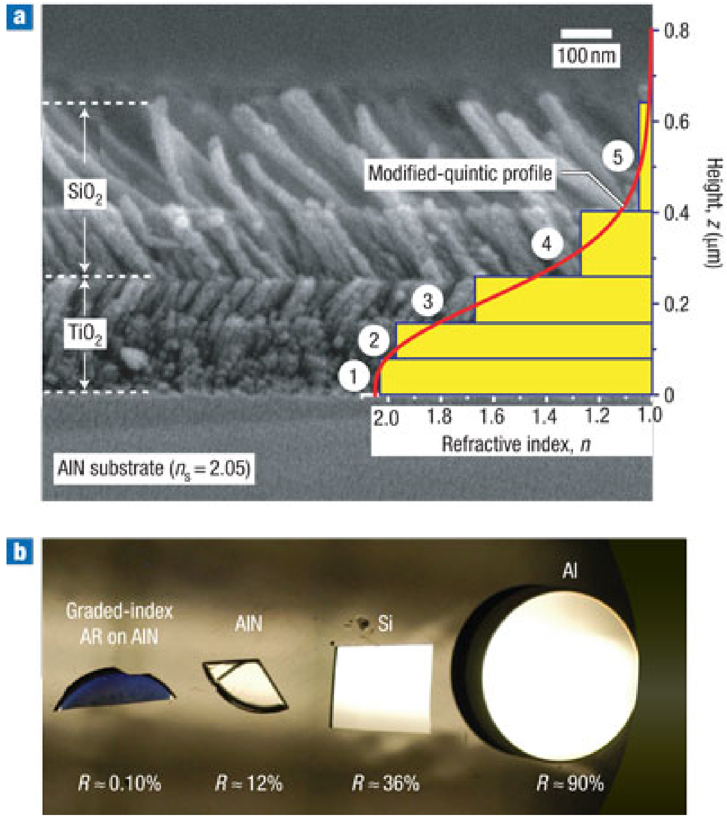
Even sophisticated issue

Graded index thin-films with low refractive index for broadband elimination of Fresnel reflection:
AR coatings for LEDs, DBRs, …



TiO_2 and SiO graded-index films deposited by oblique-angle deposition:

•This is achieved by controlling the refractive index of the TiO_2 and SiO_2 nanorod layers, down to a minimum value of n = 1.05 in the case of the latter, the lowest value so far reported.



J.-Q. Xi, Martin F. Schubert, Jong Kyu Kim, E. Fred Schubert, Minfeng Chen, Shawn-Yu Lin, W.Liu and J. Smart, *Nature Photonics* 1, 176 –79 (2007)

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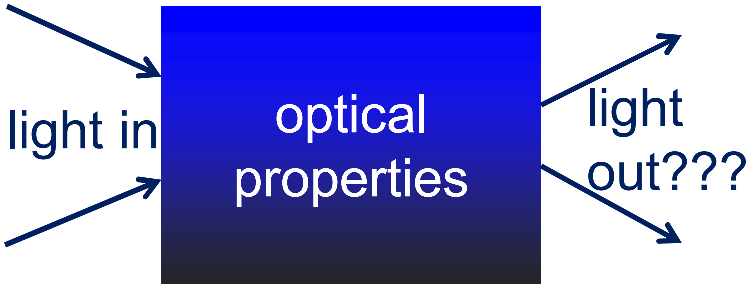
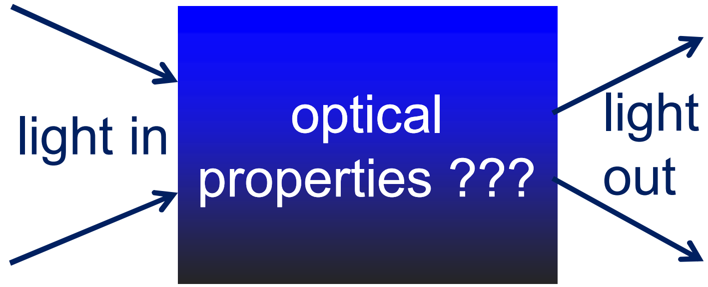
Photonics and measurement

1. **Analysis** – optical properties determination and their correlation to microstructure
2. **Synthesis** – design a microstructure to get desired optical properties

Forward problem



Inverse problem



Two models:

- System of homogeneous/inhomogeneous layers
- Effective medium approximations (EMA) - useful for porous or rough layers

Electro-optical non-destructive characterization

Method	Application
Photoluminiscence	Band gap energy, defect identification
Minority carrier lifetime spectroscopy	Lifetimes of minority carriers, surface recombination, recombination mechanisms
FTIR and Raman spectroscopies/-photometries	Chemical composition, concentration of impurities and additives, inhomogeneities
Capacitance measurements	Carrier concentration profiles, interface states, deep levels
Spectral ellipsometry	Layer thickness, crystallinity, roughness, optical and electronic properties
Scanning mapping techniques	Dislocations and grain boundaries distribution
Reflectance/transmittance spectroscopies/-photometries	Absorption spectrum, band gap energy, refractive index, surface roughness, layer thickness

Optical properties of materials

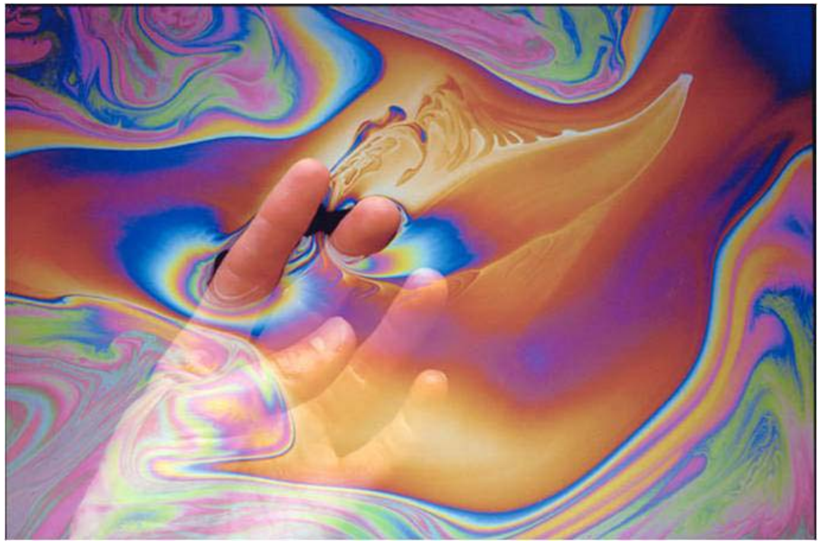
The interaction of light with matter:

Elastic scattering - energy of light is unchanged upon interaction with material

Inelastic scattering – a change in energy of light due to its interaction with the material occurs

Elastic scattering	Inelastic scattering
Reflectance Transmittance /Absorbance	Fluorescence Non-linear optics, e.g. Multi-photon absorption Frequency doubling Raman & Brillouin scattering Parametric downconversion

Optical properties of thin films arise from interference and reflection:



Optical properties of thin films arise from reflection and interference

Optical constants – parameters

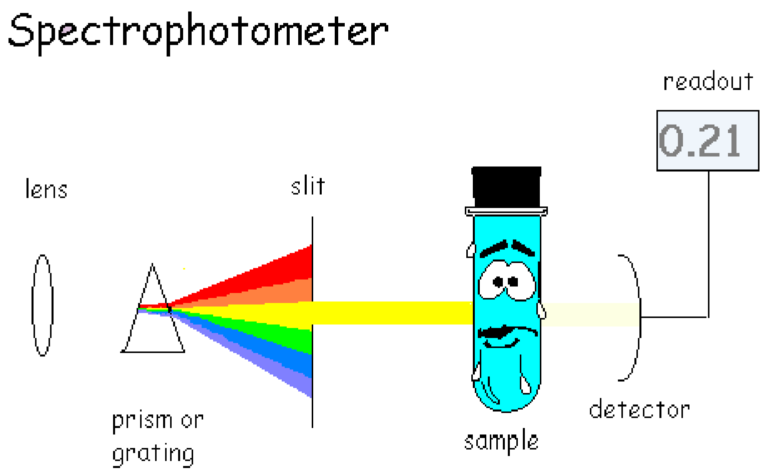
- refractive index *n* and extinction coefficient *k*
- **complex refractive index *N* = *n* – i *k***
- *n* and *k* and Kramers-Kronig relations

Dispersion relations $n(E)$, $k(E)$, $E = hc/\lambda$

- Cauchy,Sellmeier, Gladstone-Dale
- semiconductors –Tauc-Lorentz, Forouhi-Bloomer, Wemple-DiDomenico, Jelisson-Modine

Manifestation of *n, k*

- **Reflectance, transmittance, absorbance**…



www.labmonster.com

Qualitative physics: A denser material tends to have a larger refractive index because more electric dipoles will be activated when exposed to an electric field
Quantitative physics: the Lorentz-Lorenz relation
Consequences: mixing rules

Specord 210 BU http://sem.ntc.zcu.cz

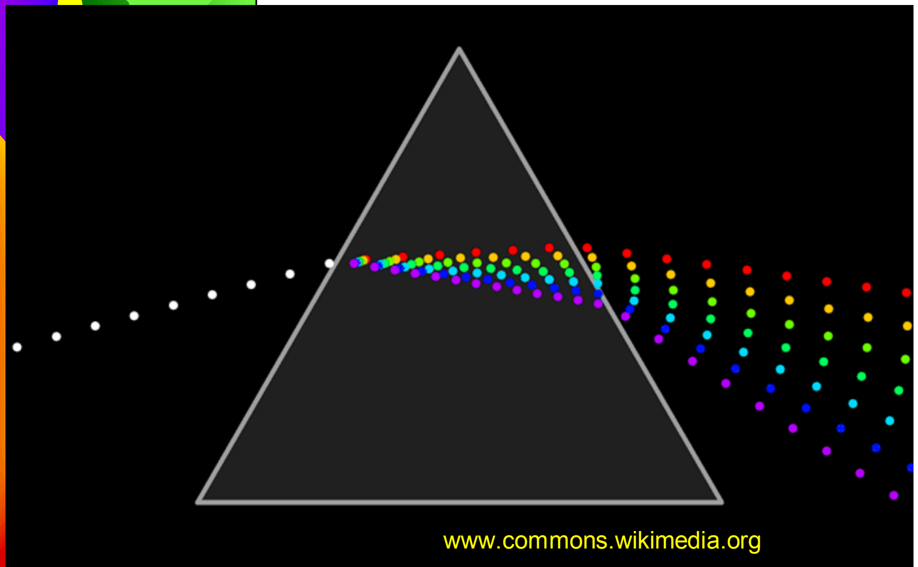
Dispersion relations

Dispersion relations $n(E)$, $k(E)$, $E = hc/\lambda$

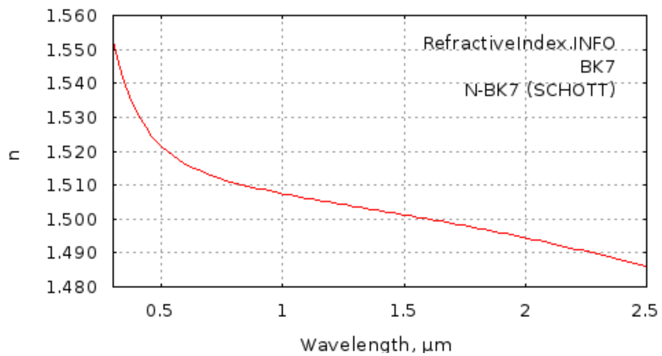
- Transparent dielectrics – Cauchy, Sellmeier, Gladstone-Dale, e.g. glasses

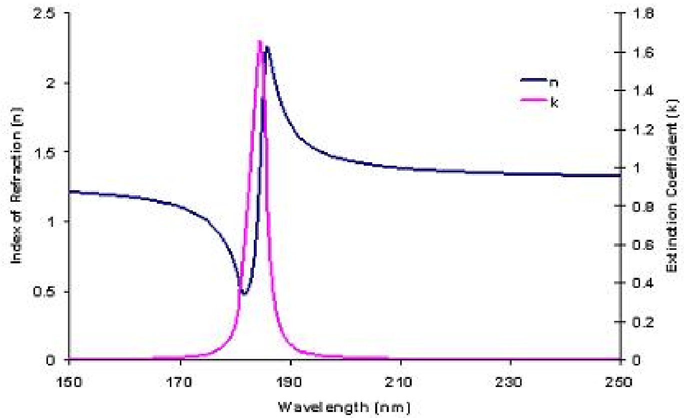
$$n^2(\lambda) = 1 + \frac{B_1\lambda}{\lambda - C_1} + \frac{B_2\lambda}{\lambda - C_2} + \frac{B_3\lambda}{\lambda - C_3}$$

- Semiconductors – Tauc-Lorentz, Forouhi-Bloomer, Wemple-DiDomenico, Jelisson-Modine



www.refractiveindex.info





Dispersion generated by Lorentz model, http://willson.cm.utexas.edu

Optical properties

- non-magnetic materials $\mu_r \approx 1$
- complex refractive index $N = n - i\,k$ $\quad \hat{n}_\iota = \sqrt{\hat{\varepsilon}_\iota}$
- n … refractive index, k … extinction coefficient

$$n = \left[\frac{\left(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega)\right)}{2}\right]^{1/2} \qquad k = \left[\frac{\left(\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)\right)}{2}\right]^{1/2}$$

Electric field strength($V \cdot m^{-1}$)

$$\vec{E} = \vec{E}_0 \exp\left\{i\left[\omega\tau - \frac{2\pi(n - ik)}{\lambda} z\right]\right\}$$

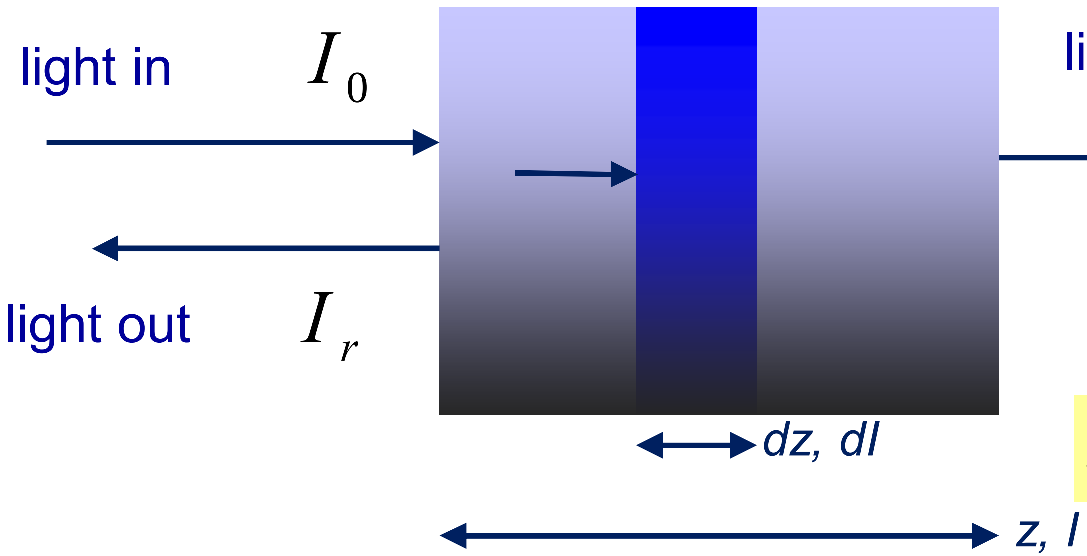
Intensity of light ($W \cdot m^{-2}$) $I \sim \left\langle |E|^2 \right\rangle = E_0^2 \exp\left(-\frac{4\pi k}{\lambda} z\right) = E_0^2 \exp(-\alpha z)$

Absorption coefficient (cm^{-1})

$$\alpha = \frac{4\pi k}{\lambda}$$

Reflection & refraction of light at a boundary- Fresnel relations

Macroscopic view



$$dI = -\alpha I dz$$

$$I = I_0 \exp(-\alpha z)$$

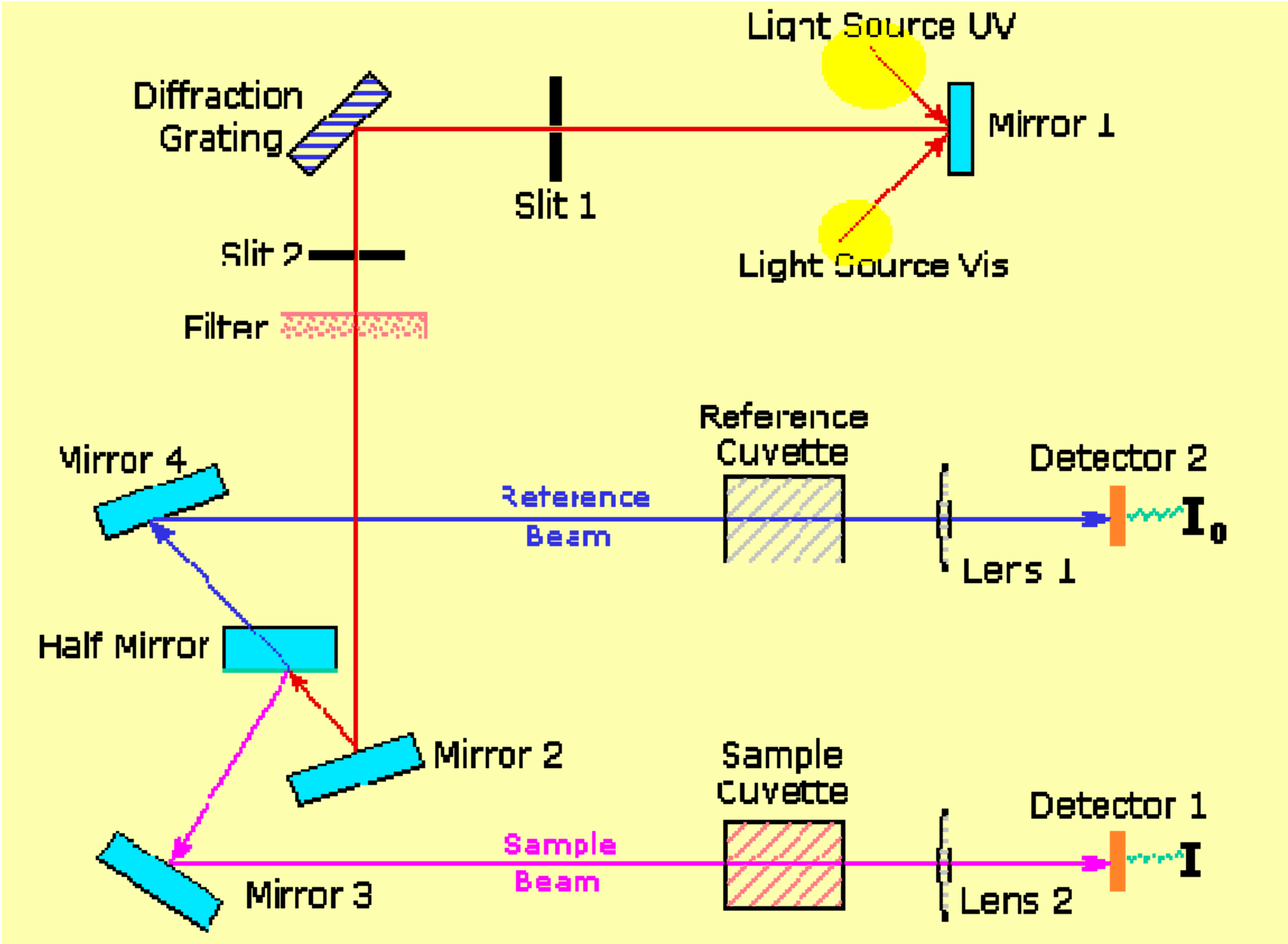
α **= absorption coefficient (cm^{-1})**

Reflectance *R*, transmittance *T*, absorbance *A*:
the ratio of reflected, transmitted or absorbed radiant power (light intensity) to incident power

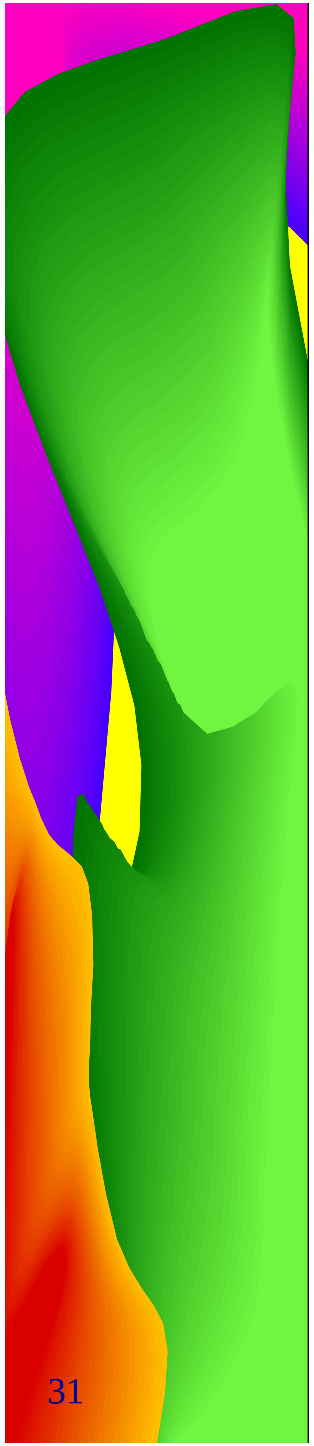
Conservation law: $R + T + A = 1$

(blackbody *A* =1, *R* = *T* = 0, opaque surface *A* +*R* =1)

Spectrophotometry



http://bricker.tcnj.edu/tech



Light absorption: Beer's law

… (Beer-Lambert, Beer-Lambert-Bouguer) relates the light absorption to the material properties

Transmittance $T = \frac{I}{I_0} = 10^{-\alpha' z}$ **or** $T = \frac{I}{I_0} = e^{-\alpha z}$

α **= molar (decadic) absorption coefficient**

Absorption … transformation of radiant power *P* to another type of energy – e.g. heat, light - by interaction with matter.

Gases or liquids (reflectance negligible):

$$A' = -\log_{10} \frac{I}{I_0} = \alpha' z = \varepsilon c z$$

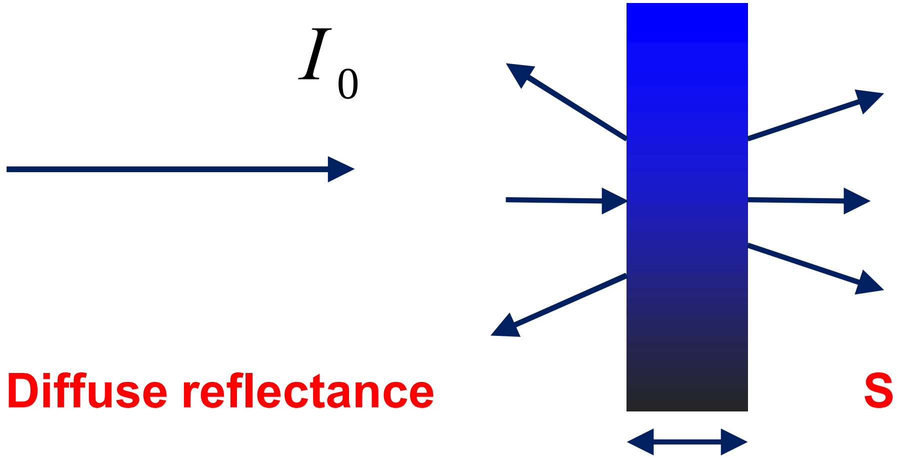
ε is the molar absorptivity (l·mol $^{-1}$ ·cm $^{-1}$) or extinction coeff.
c is the concentration of the compound in the solution (l $^{-1}$ · mol)

$$A = -\ln \frac{I}{I_0} = \alpha z = \sigma N z$$

σ is the absorption cross section (m^2)
N is the density of absorbing particles (m $^{-3}$)

Dispersion generated by Lorentz model, http://willson.cm.utexas.edu

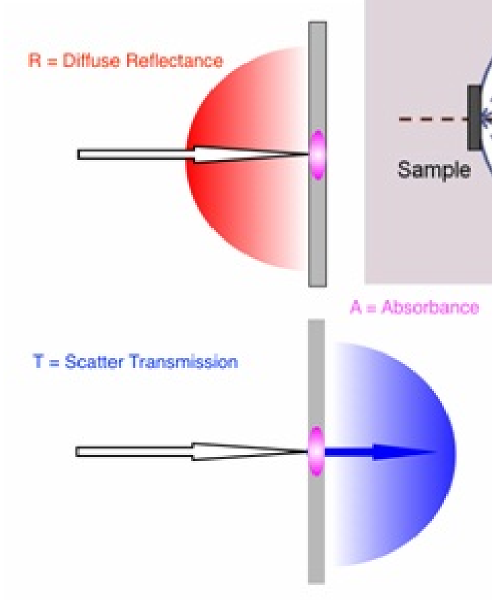
Absorption vs. scattering

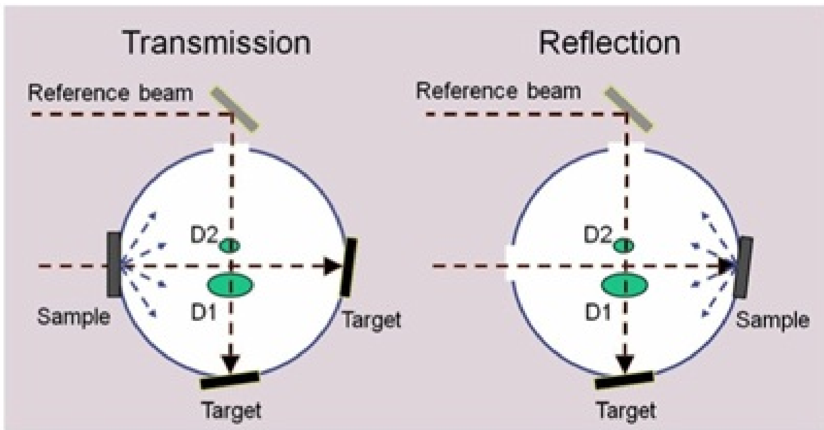


$$\alpha = \alpha_{abs} + \alpha_{scatt}$$

Scatter transmittance

Spectrophotometer with **integrating sphere**





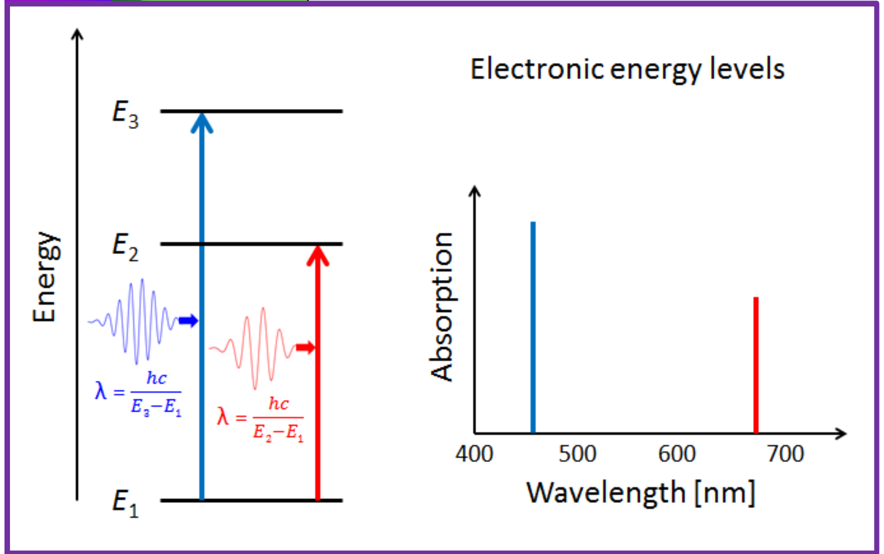
www.azonano.com

Absorption: microscopic view

Spectroscopy:

- the analysis of absorption or emission of electromagnetic radiation by molecules of the sample (radiative transitions between energy states)
- energy states – electronic, vibrational, rotational
- enables to determine structure, symmetry, energy levels etc.

Energies are quantized !



Born-Oppenheimer approximation:

- the assumption that the electronic motion and nuclear motion in a molecule can be separated, then the wave function

$$\psi_{molecule} = \psi_{electrons}(\vec{r}_i, \vec{R}_j)\psi_{nuclei}(\vec{R}_j)$$

$$\hat{H} = \hat{H}_{electron} + \hat{H}_{nuclei}$$

- due to the mass: the nuclear motion - much slower than the electron motion – separation of vibrational, translational and rotational motions
- **the eigenvalue of the Hamiltonian - internal energy of a molecule:**

$$E = E_{el} + E_{nucl} = E_{el} + E_{vib} + E_{rot}$$

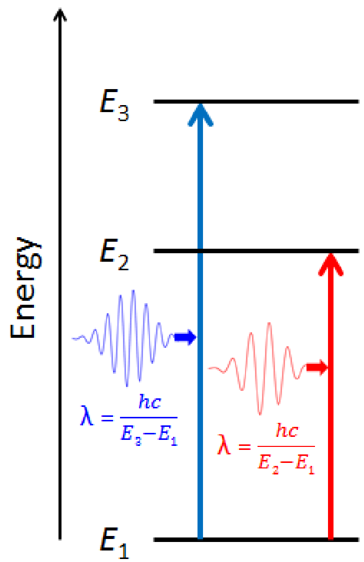
Born-Oppenheimer approximation

$$E = E_{el} + E_{vib} + E_{rot}$$

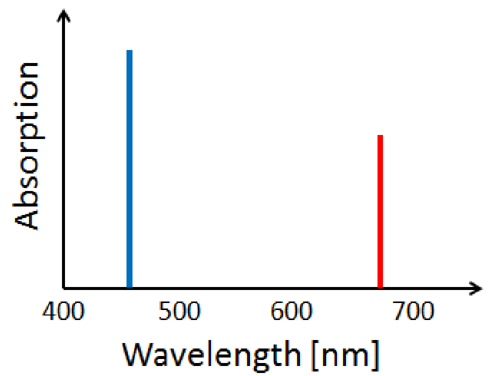
www.tau.ac.il

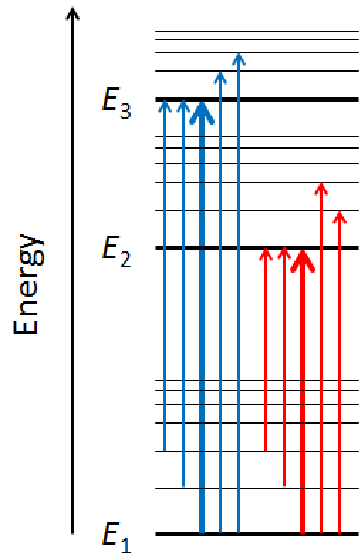
Ro-vibrational fine structure:

$$E_{el} >> E_{vib} >> E_{rot}$$

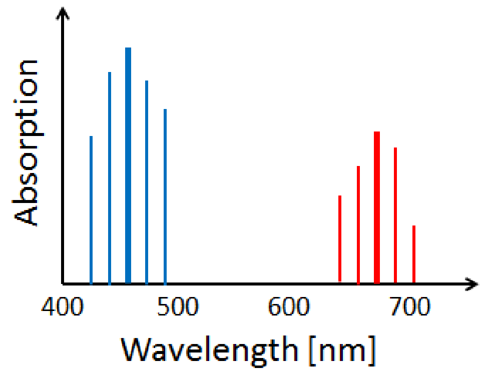


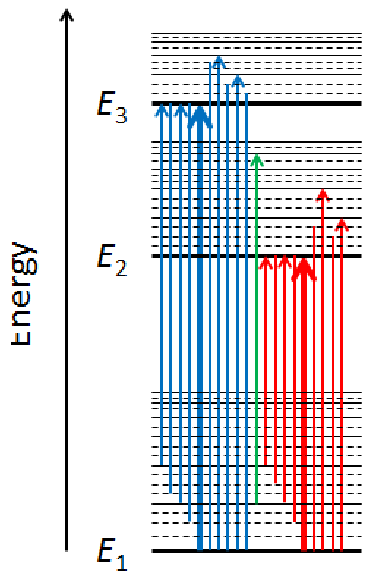
Electronic energy levels



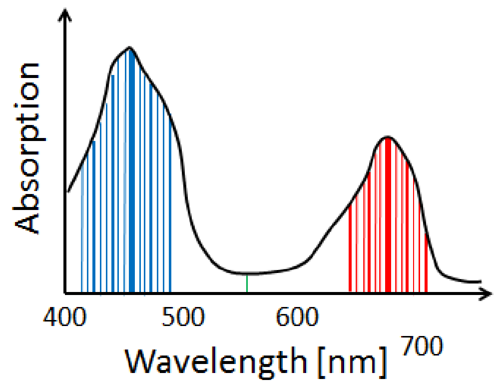


Electronic + vibrational energy levels





Electronic + vibrational + rotational energy levels



www.ocenopticsbook.info

Absorption and emission

Spectroscopy:

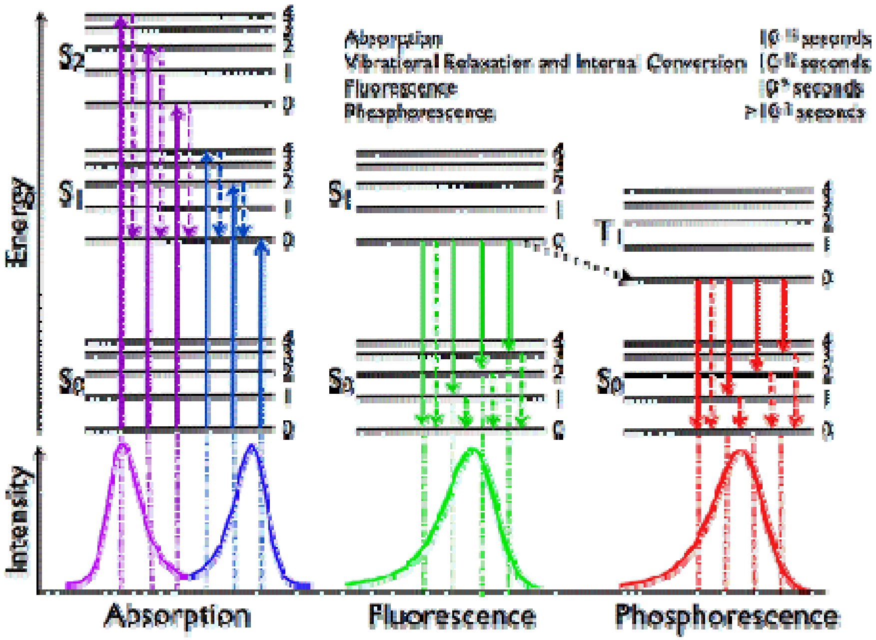
- the analysis of absorption or emission of electromagnetic radiation by the sample (radiative transitions between energy states)
- energy states – electronic, vibrational, rotational
- enables to determine structure, symmetry, energy levels etc.

Internal energy of a molecule:

$$E \approx E_{el} + E_{vib}$$

www.tau.ac.il

Jablonski diagram:



luminiscence

Alexander Jablonski, 1898-1980

Franck-Condon principle

… describes the intensities of vibronic (= electronic+vibrotional) transitions connected with the absorption or emission of a photon

... when a molecule is undergoing an electronic transition, the nuclear configuration of the molecule does not change significantly (due to the fact that nuclei are much more massive than electrons the electronic transition takes place faster than the nuclei can respond)

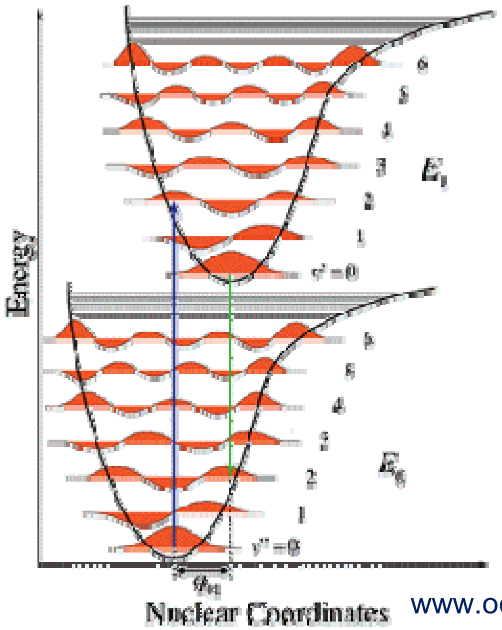
… the nucleus must undergo a vibration when it realigns itself with the new electronic configuration

… on a potential energy diagram the most likely transitions are vertical transitions

…

James Franck, 1882 – 1964, Nobel Laureate 1925

Edward Condon, 1902 – 1974



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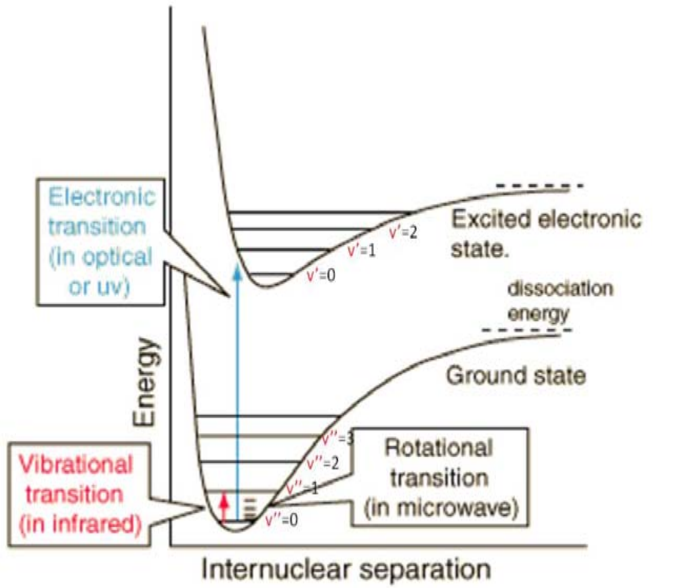

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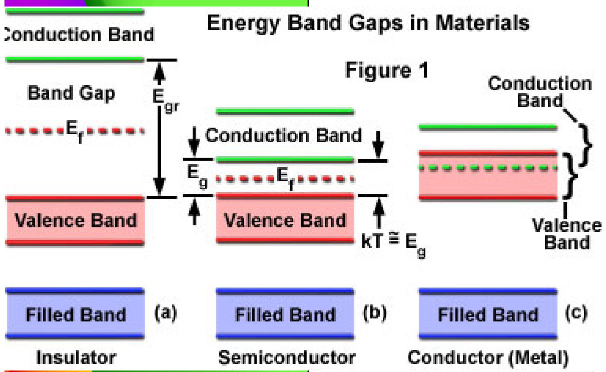
Electronic band structure

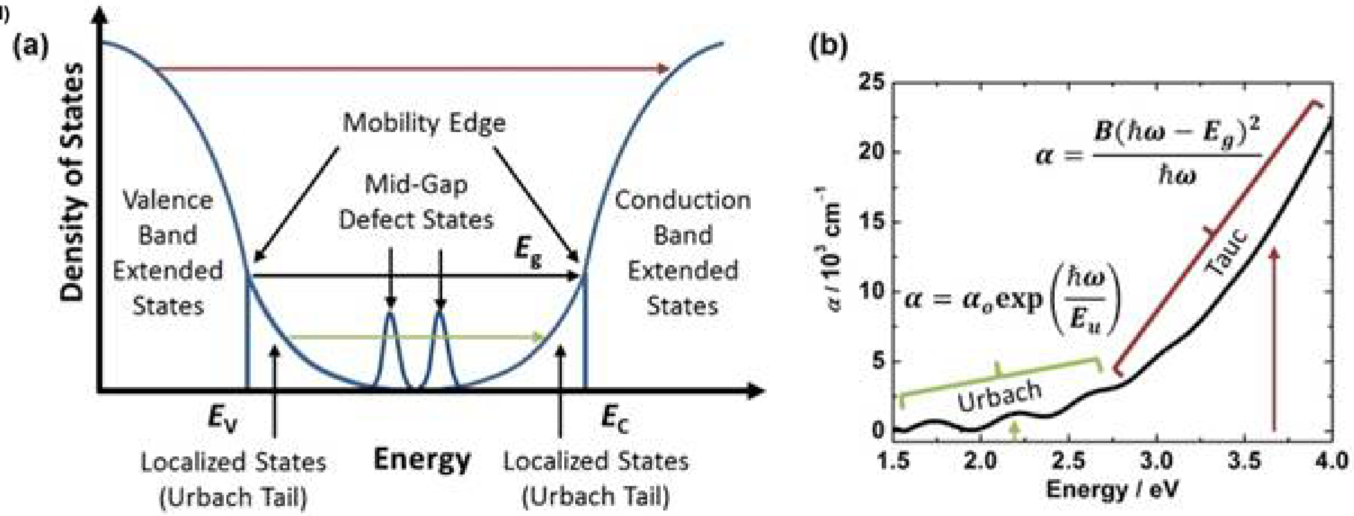
- Solids - interaction of very large number of atoms – energy levels closely spaced forming bands
- Valence band – analogous to highest occupied molecular orbital in a molecule HOMO
- Conduction band – analogous to the lowest unoccupied molecular orbital LUMO
- Band gap (energy gap) – the energy separation between them



www2.warwick.ac.uk

Amorphous semiconductors- simplified density of states and absorption coefficient vs. photon energy

Tail states… the question on band gap and optical band gap ?



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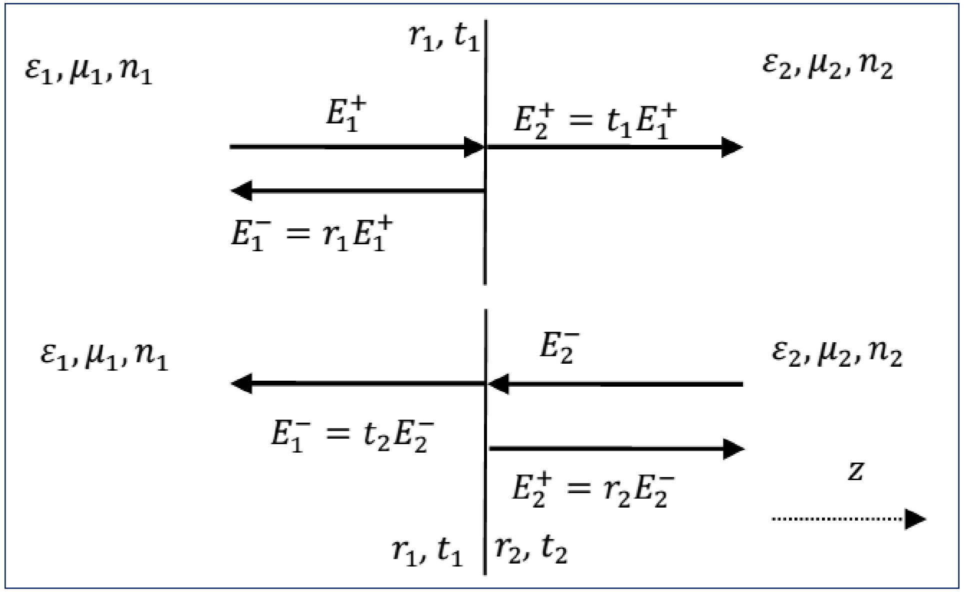
Optics on a media boundary



Boundary conditions - tangential components continuity for electric and magnetic field:

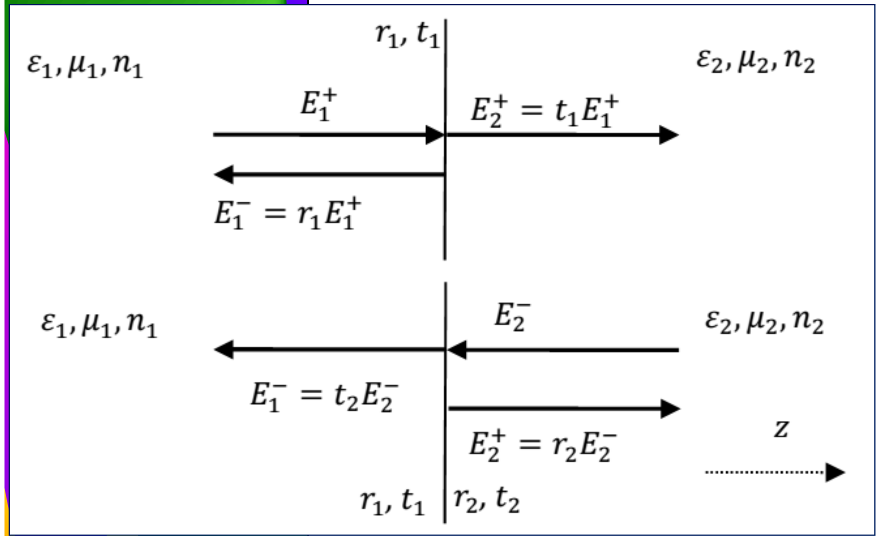
$$E_1^+ + E_1^- = E_2^+ + E_2^-$$

$$\sqrt{\frac{\varepsilon_1}{\mu_1}}(E_1^+ - E_1^-) = \sqrt{\frac{\varepsilon_2}{\mu_2}}(E_2^+ - E_2^-)$$

or

$$E_1^+ - E_1^- = \frac{n_2}{n_1}E_2^+ - \frac{n_2}{n_1}E_2^-$$

Matrix method – an interface



$$E_1^+ + E_1^- = E_2^+ + E_2^-$$

$$E_1^+ - E_1^- = \frac{n_2}{n_1} E_2^+ - \frac{n_2}{n_1} E_2^-$$

$$\begin{bmatrix} E_1^+ \\ E_1^- \end{bmatrix} = \frac{1}{2n_1} \begin{bmatrix} n_1 + n_2 & n_1 - n_2 \\ n_1 - n_2 & n_1 + n_2 \end{bmatrix} \begin{bmatrix} E_2^+ \\ E_2^- \end{bmatrix} =$$

$$= \frac{n_1 + n_2}{2n_1} \begin{bmatrix} 1 & \dfrac{n_1 - n_2}{n_1 + n_2} \\ \dfrac{n_1 - n_2}{n_1 + n_2} & 1 \end{bmatrix} \begin{bmatrix} E_2^+ \\ E_2^- \end{bmatrix}$$

$$E_1^+ = \frac{1}{t_1} E_2^+ + \frac{r_2}{t_1} E_2^-$$

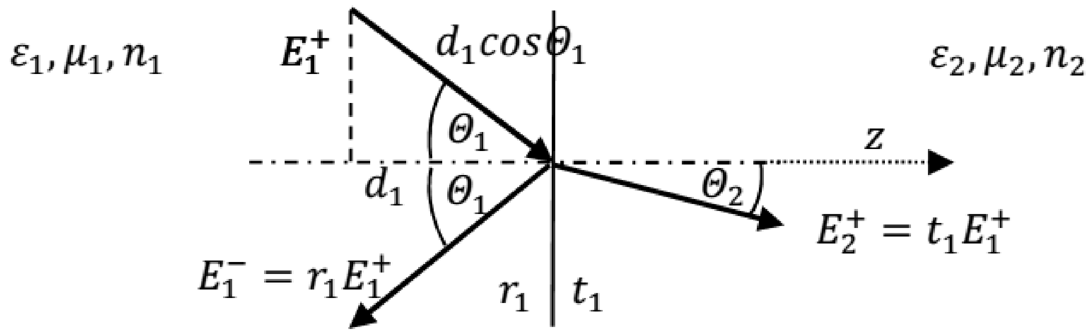
$$E_1^- = \frac{r_1}{t_1} E_2^+ + \frac{1}{t_1} E_2^-$$

$$t_1 = \frac{2n_1}{n_1 + n_2}$$

$$r_1 = \frac{n_1 - n_2}{n_1 + n_2}$$

$$\begin{bmatrix} E_1^+ \\ E_1^- \end{bmatrix} = \frac{1}{t_1} \begin{bmatrix} 1 & r_1 \\ r_1 & 1 \end{bmatrix} \begin{bmatrix} E_2^+ \\ E_2^- \end{bmatrix}$$

Oblique incidence



Fresnel's equations:

$$r_s = \left(\frac{E_1'}{E_1}\right)_s = \frac{n_1 cos\Theta_1 - n_2 cos\Theta_2}{n_1 cos\Theta_1 + n_2 cos\Theta_2}$$

$$r_p = \left(\frac{E_1'}{E_1}\right)_p = \frac{n_2 cos\Theta_1 - n_1 cos\Theta_2}{n_2 cos\Theta_1 + n_1 cos\Theta_2}$$

$$t_s = \left(\frac{E_2}{E_1}\right)_s = \frac{2 n_1 cos\Theta_1}{n_1 cos\Theta_1 + n_2 cos\Theta_2}$$

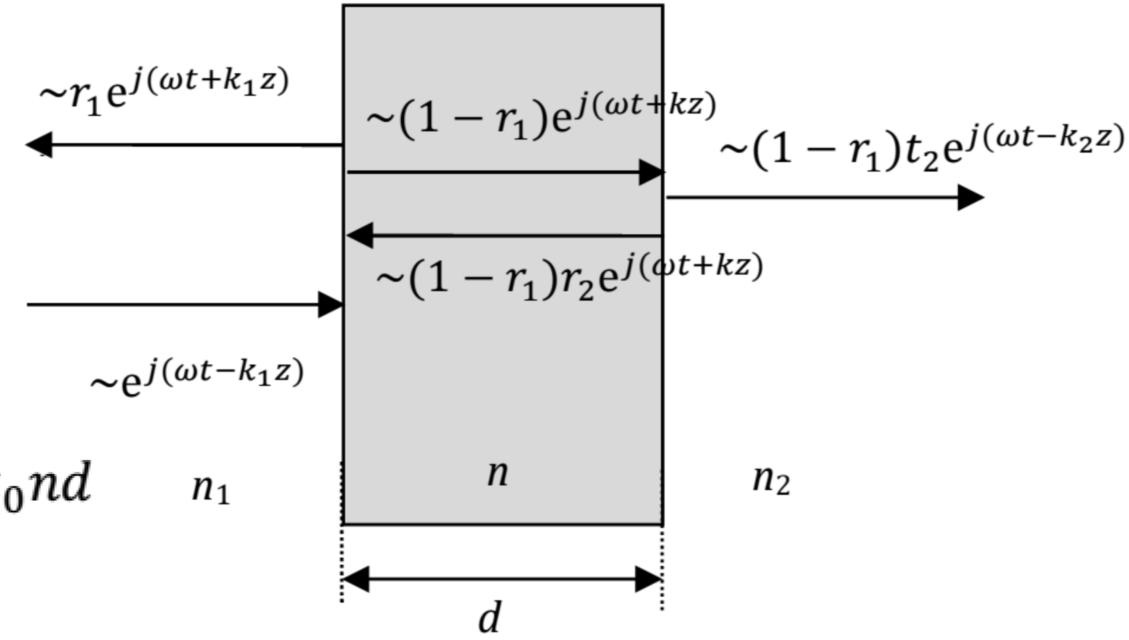
$$t_p = \left(\frac{E_2}{E_1}\right)_p = \frac{2 n_1 cos\Theta_1}{n_2 cos\Theta_1 + n_1 cos\Theta_2}$$

$$R_{s,p} = \left(\frac{I_1'}{I_1}\right)_{s,p} = (r)_{s,p}^2$$

$$T_{s,p} = \left(\frac{I_1' cos\Theta_2}{I_1 cos\Theta_1}\right)_{s,p} =$$

$$= \frac{n_2}{n_1}\left(\frac{E_2}{E_1}\right)_{s,p}^2 \frac{cos\Theta_2}{cos\Theta_1} = \frac{n_2}{n_1}\frac{cos\Theta_2}{cos\Theta_1}(t)_{s,p}^2$$

One single layer: two interfaces



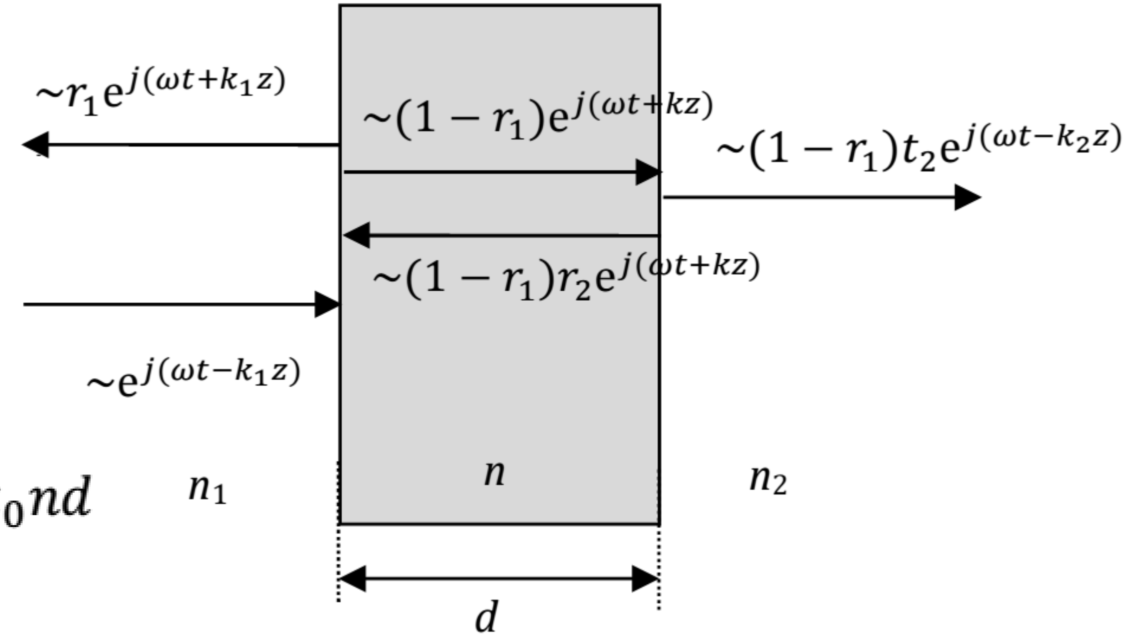
$$kd = \frac{2\pi}{\lambda} d = k_0 n d$$

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = \frac{1}{t_1} \begin{bmatrix} 1 & r_1 \\ r_1 & 1 \end{bmatrix} \begin{bmatrix} e^{jkd} & 0 \\ 0 & e^{-jkd} \end{bmatrix} \frac{1}{t_2} \begin{bmatrix} 1 & r_2 \\ r_2 & 1 \end{bmatrix} \begin{bmatrix} E_2^+ \\ 0 \end{bmatrix}$$

$$t_1 = \frac{2n_1}{n_1 + n} \qquad t_2 = \frac{2n}{n_2 + n}$$

$$r_1 = \frac{n_1 - n}{n_1 + n} \qquad r_2 = \frac{n - n_2}{n + n_2}$$

One single layer



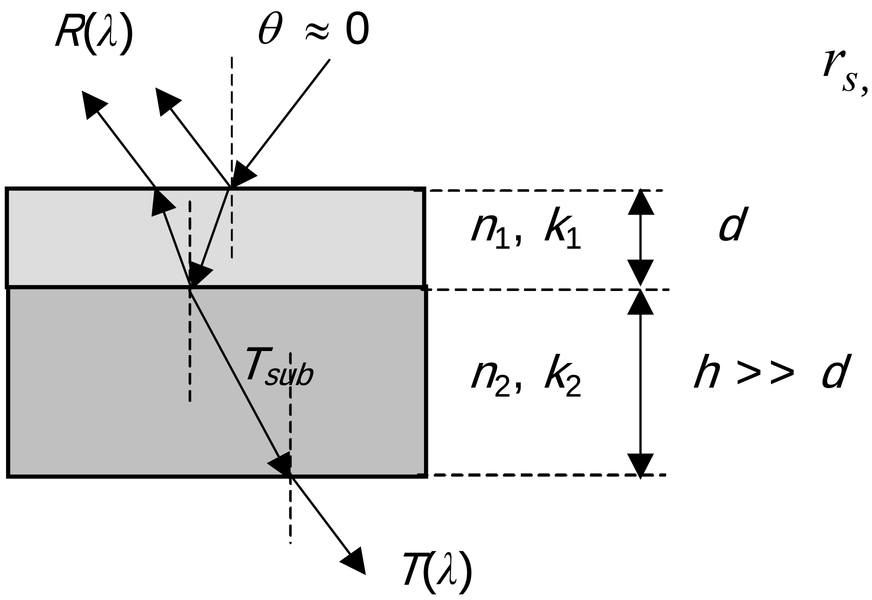
$$kd = \frac{2\pi}{\lambda} d = k_0 n d$$

$$\begin{bmatrix} E_0^+ \\ E_0^- \end{bmatrix} = \frac{1}{t_1 t_2} \begin{bmatrix} e^{jkd} + r_1 r_2 e^{-jkd} & r_2 e^{jkd} + r_1 e^{-jkd} \\ r_1 e^{jkd} + r_2 e^{-jkd} & r_1 r_2 e^{jkd} + e^{-jkd} \end{bmatrix} \begin{bmatrix} E_2^+ \\ 0 \end{bmatrix}$$

$$r = \frac{E_0^-}{E_0^+} = \frac{r_1 e^{jkd} + r_2 e^{-jkd}}{e^{jkd} + r_1 r_2 e^{-jkd}} = \frac{r_1 + r_2 e^{-2jkd}}{1 + r_1 r_2 e^{-2jkd}}$$

$$t = \frac{E_2^+}{E_0^+} = t_1 t_2 \frac{1}{e^{jkd} + r_1 r_2 e^{-jkd}} = \frac{t_1 t_2 e^{-jkd}}{1 + r_1 r_2 e^{-2jkd}}$$

A thin film on a thick substrate



$$r_{s,p} = \frac{r_{01s,p} + r_{12s,p}\exp(-2i\delta)}{1 + r_{01s,p} r_{12s,p}\exp(-2i\delta)}$$

$$\delta = \frac{2\pi d N_1}{\lambda}$$

$$r_{01s,p} = \pm\frac{1 - N_1}{1 + N_1}$$

$$r_{12s,p} = \pm\frac{N_1 - N_2}{N_1 + N_2}$$

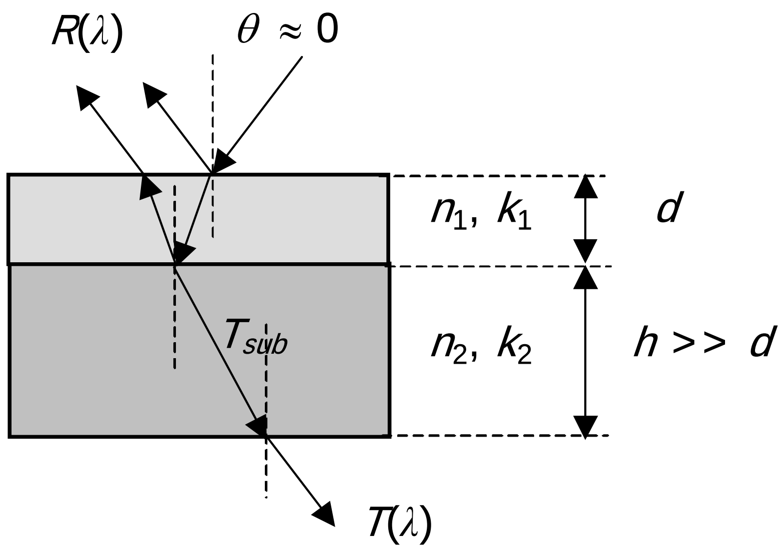
R … reflectance

r … Fresnel amplitude

$$R = |r|^2 \qquad R_{s,p} = |r_{s,p}|^2$$

One layer reflectance

$$R = \frac{A + Bx + Cx^2}{D + Ex + Fx^2}$$



$$A = \left[(1-n_1)^2 + k_1^2\right]\left[(n_1+n_2)^2 + (k_1+k_2)^2\right]$$

$$C = \left[(1+n_1)^2 + k_1^2\right]\left[(n_1-n_2)^2 + (k_1-k_2)^2\right]$$

$$D = \left[(1+n_1)^2 + k_1^2\right]\left[(n_1+n_2)^2 + (k_1+k_2)^2\right]$$

$$F = \left[(1-n_1)^2 + k_1^2\right]\left[(n_1-n_2)^2 + (k_1-k_2)^2\right]$$

$$B = 2\left[A'\cos\varphi + B'\sin\varphi\right]$$

$$E = 2\left[C'\cos\varphi + D'\sin\varphi\right]$$

$$x = \exp(-\alpha d)$$

$$A' = \left(1 + n_1^2 - k_1^2\right)\left(n_1^2 - n_2^2 + k_1^2 - k_2^2\right) + 4k_1\left(n_1 k_2 - n_2 k_1\right) \qquad \alpha = \frac{4\pi k}{\lambda}$$

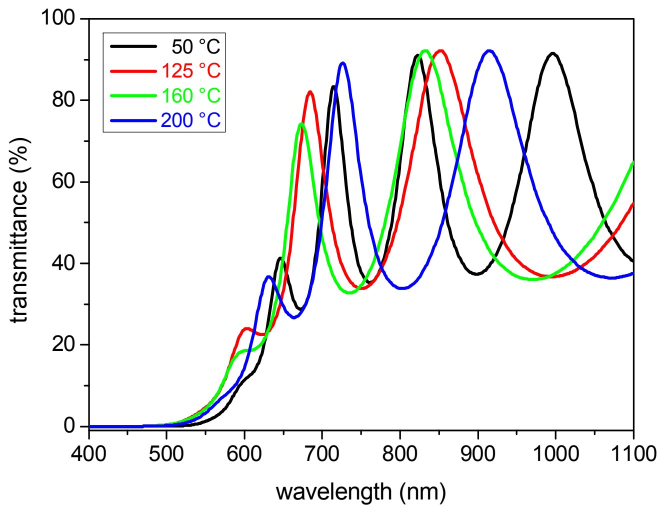
$$C' = \left(1 - n_1^2 - k_1^2\right)\left(n_1^2 - n_2^2 + k_1^2 - k_2^2\right) - 4k_1\left(n_1 k_2 - n_2 k_1\right)$$

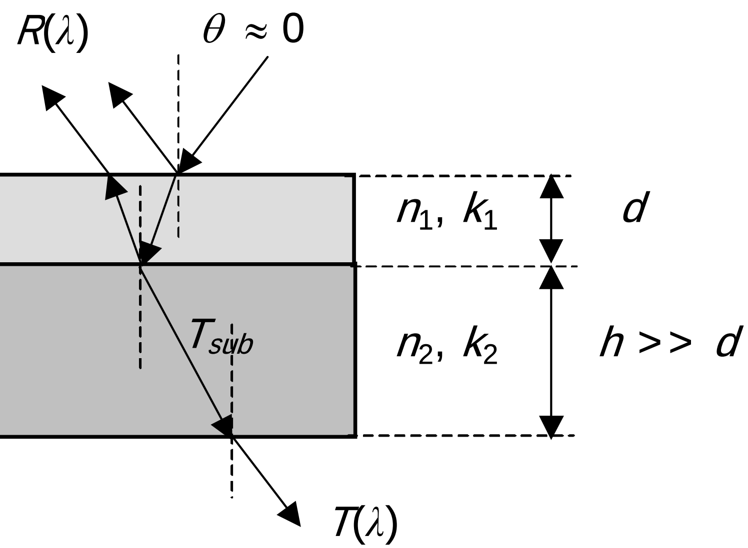
$$B' = 2\left(1 + n_1^2 - k_1^2\right)\left(n_1 k_2 - n_2 k_1\right) - 2k_1\left(n_1^2 - n_2^2 + k_1^2 - k_2^2\right) \qquad \varphi = \frac{4\pi n_1 d}{\lambda}$$

$$D' = 2\left(1 - n_1^2 - k_1^2\right)\left(n_1 k_2 - n_2 k_1\right) + 2k_1\left(n_1^2 - n_2^2 + k_1^2 - k_2^2\right)$$

One layer transmittance

$$T = \frac{A}{B - Cx + Dx^2}$$





$$x = \exp(-\alpha d)$$

$$A = 16 n_2 \left(n_1^2 + k_1^2\right)$$

$$B = \left[(1 + n_1)^2 + k_1^2\right]\left[\left(n_1 + n_2^2\right)(n_1 + 1) + k_1^2\right]$$

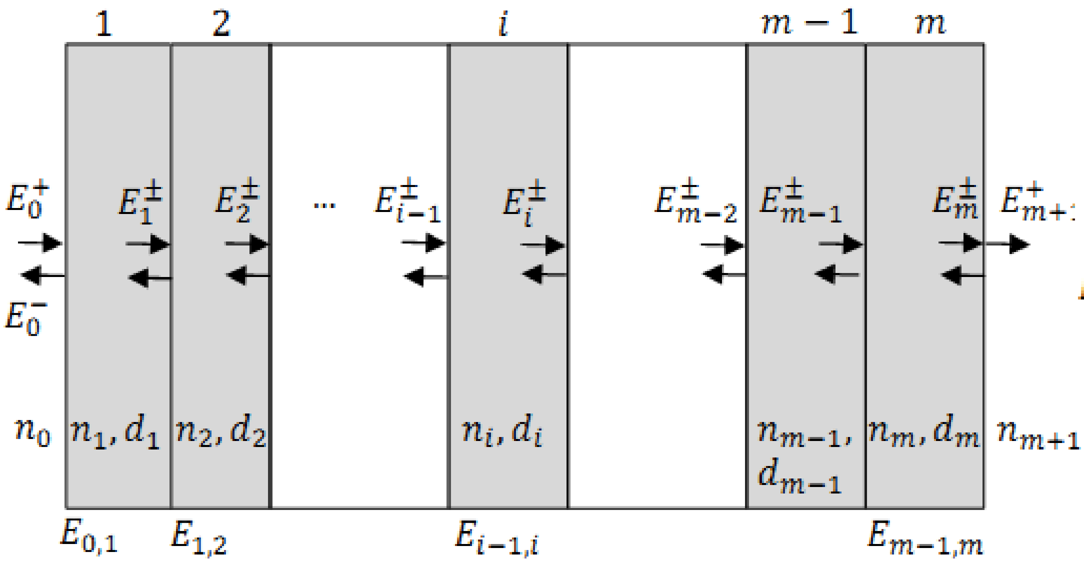
$$C = 2\cos\varphi\left[\left(n_1^2 + k_1^2 - 1\right)\left(n_1^2 + k_1^2 - n_2^2\right) - 2k_1^2\left(n_1^2 + 1\right)\right] - 2\sin\varphi\left[\left(n_1^2 + k_1^2 - 1\right)\left(n_2^2 + 1\right) + 2\left(n_1^2 + k_1^2 - n_2^2\right)\right]$$

$$D = \left[(n_1 - 1)^2 + k_1^2\right]\left[(n_1 - 1)\left(n_1 - n_2^2\right) + k_1^2\right]$$

$$\alpha = \frac{4\pi k}{\lambda}$$

$$\varphi = \frac{4\pi n_1 d}{\lambda}$$

A multilayer structure



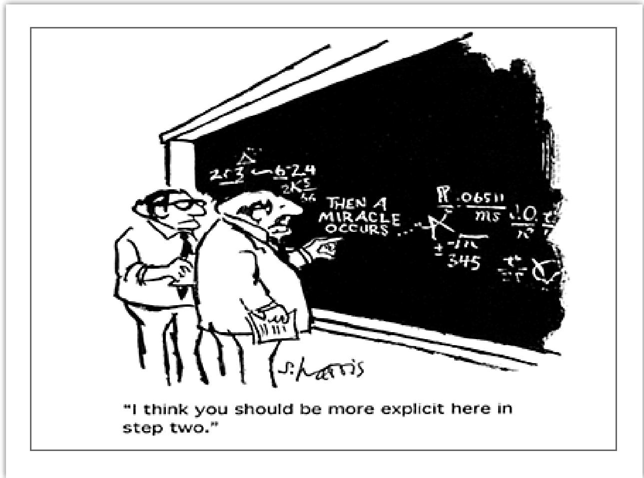
$$\tilde{M}_{i+1} = \begin{bmatrix} e^{jk_i d_i} & r_{i+1} e^{-jk_i d_i} \\ r_{i+1} e^{jk_i d_i} & e^{-jk_i d_i} \end{bmatrix}.$$

Transfer matrix

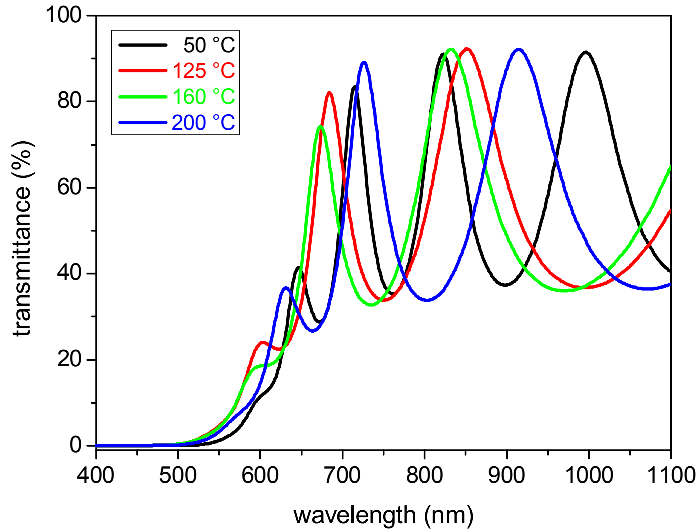
$$\tilde{M} = \frac{1}{\prod_{i=1}^{i=m+1} t_i} \tilde{M}_1 \tilde{M}_2 \ldots \tilde{M}_{i-1} \tilde{M}_i \ldots \tilde{M}_m \tilde{M}_{m+1} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix}$$

$$r = \frac{E_0^-}{E_0^+} = \frac{M_{21}}{M_{11}} \qquad t = \frac{E_{m+1}^+}{E_0^+} = \frac{1}{M_{11}}$$

Analysis – optical properties



"I think you should be more explicit here in step two."



Measurements of *R, T*:
Non-linear equations, too many independent parameters:

$$R(n_1, k_1, d, \lambda_i) - R_{\exp}(\lambda_i) = 0$$

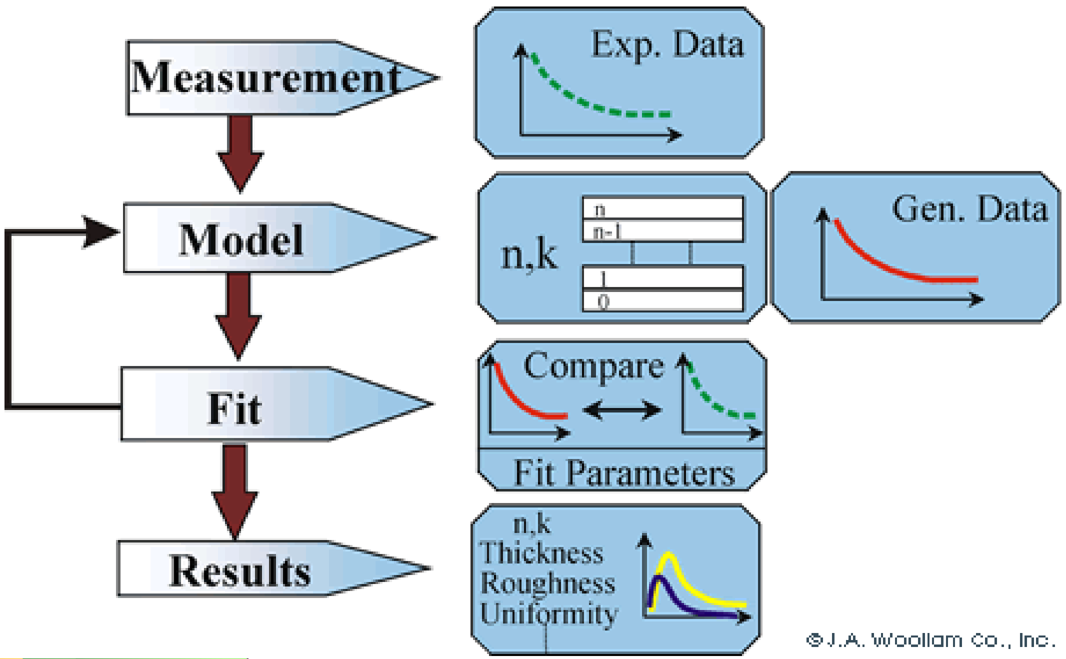
$$T(n_1, k_1, d, \lambda_i) - T_{\exp}(\lambda_i) = 0$$

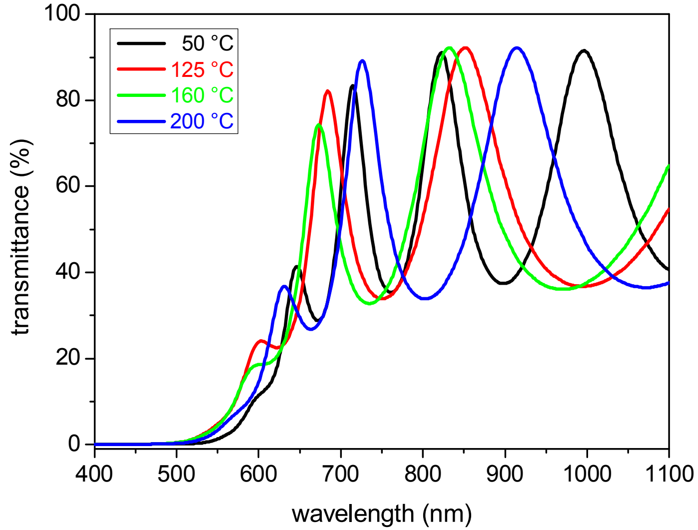
Experimental data processing:

1. Additional independent measurements
2. Non-absorbing films & specific cases – the analytical solution
3. The envelope method
4. The inversion methods:
    - Numerical solutions
    - **Optimization procedures**

$$M = \sum_{i=1}^{p} \left[R(n_1, k_1, d, \lambda_i) - R_{\exp}(\lambda_i) \right]^2$$

Numerical data analysis





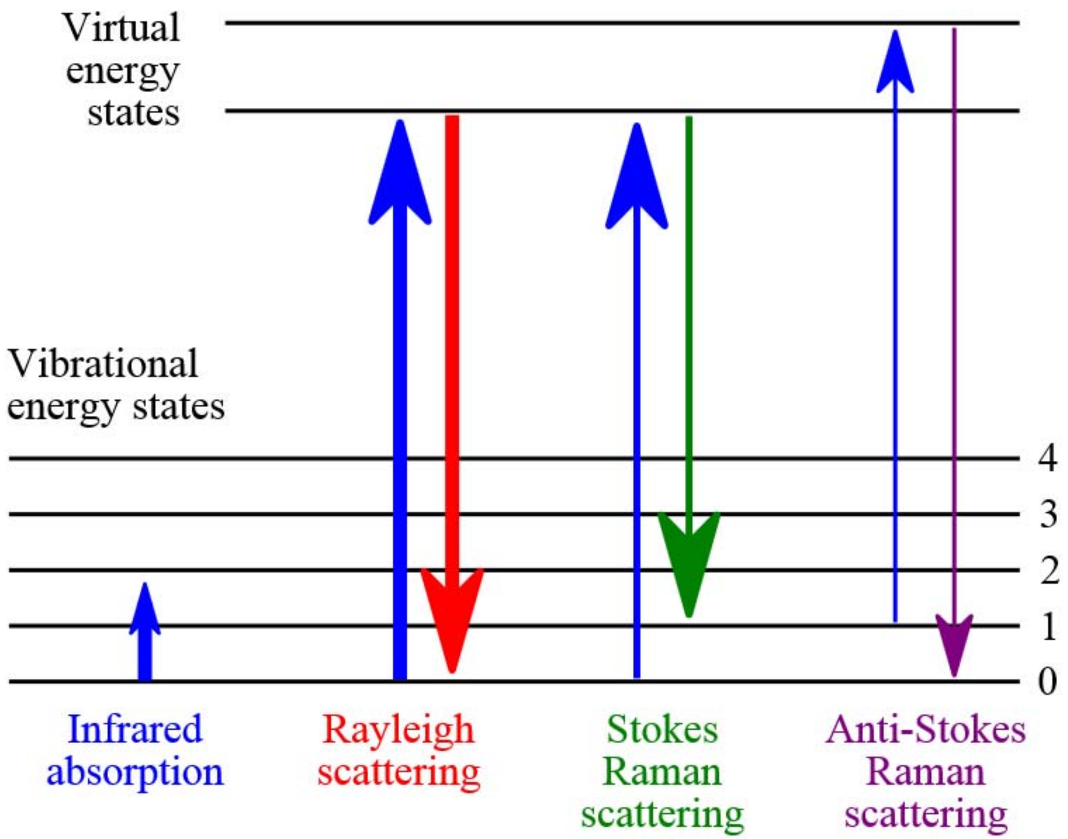
Merit function (e.g. for reflectance):

$$M = \sum_{i=1}^{p} \left[R(n_1, k_1, d, \lambda_i) - R_{\exp}(\lambda_i) \right]^2$$

Global optimization procedures: stochastic algorithms – randomness to accelerate the calculation, e.g. evolutionary algorithms (e.g. GA), simulated annealing, hill climbing, swarm algorithms (e.g. PSO, SOMA, Ant Colony) etc.

Vibrational spectroscopies

Provide information on type of bonds and partially on structure



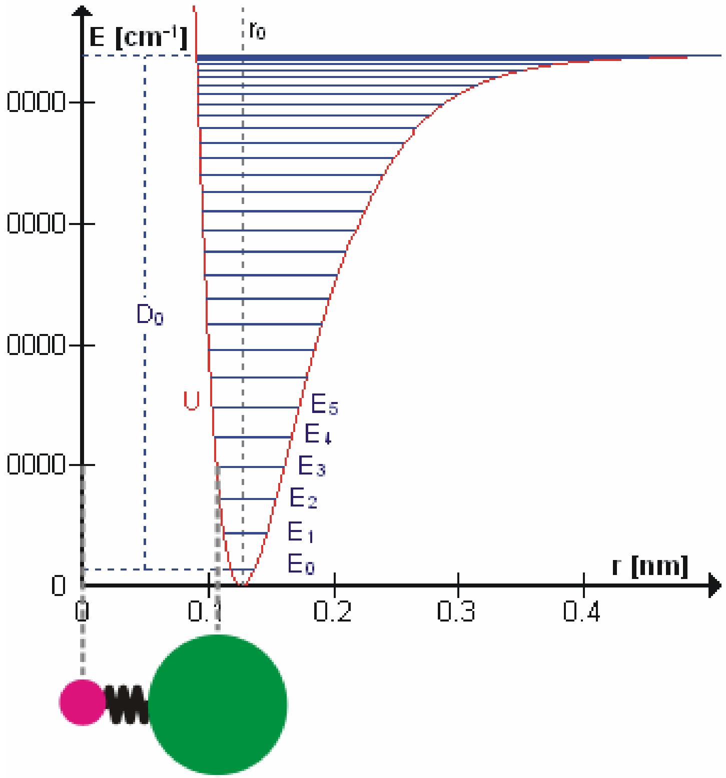
Vibrational fundamentals

Diatomic molecule: an harmonic oscillator approximation:

Vibrations obey the Hooke's law: $F = -kx$

k – the force constant, *x* – the displacement from equilibrium

Potential energy $V = \frac{kx^2}{2}$



The Schrödinger equation: $\frac{\hbar^2}{2m_{eff}}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi$

$m_{eff} = \frac{m_1 m_2}{m_1+m_2}$ the reduced mass

The solution => energies of vibrational states

$$E_{harm} = (v + \tfrac{1}{2})\hbar\omega,\ v = 0,1,2, \ldots$$

Anharmonic oscillator:

$$E_{anharm} = \left(v + \frac{1}{2}\right)\hbar\omega - \left(v + \frac{1}{2}\right)^2 \hbar\omega x_e + \ \ldots,$$

$v = 0,1,2, \ldots$

Absorption of radiation by a molecular vibration – selection rules => $\Delta v = \pm 1$ (+ absorption, - emission)

www.chemwiki.uc.davis.edu

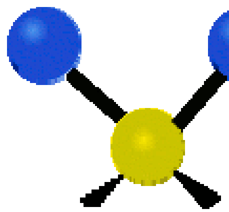
Vibrational fundamentals

Vibrational spectroscopy – useful for identification and structure determination of compounds connected with vibrational states

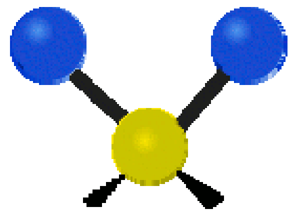
Molecular vibration modes:

Normal modes – some or all atoms vibrate together **with the same frequency** in a defined manner, their number = 3N-5 for a linear molecule, = 3N-6 for a nonlinear molecule (N = number of bonded atoms)

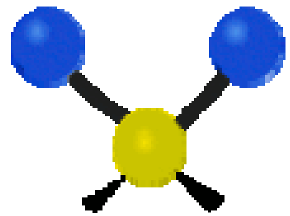
Non normal modes – expressable in terms of normal modes



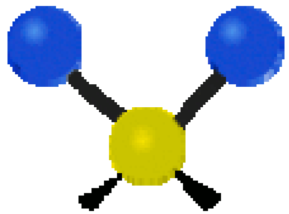
Symmetrical Stretching



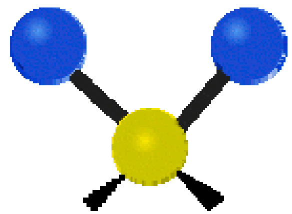
Asymmetrical Stretching



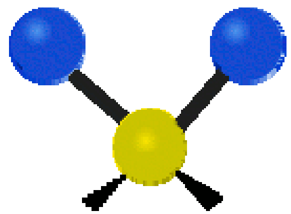
Bending (Rocking)



Bending (Twisting)



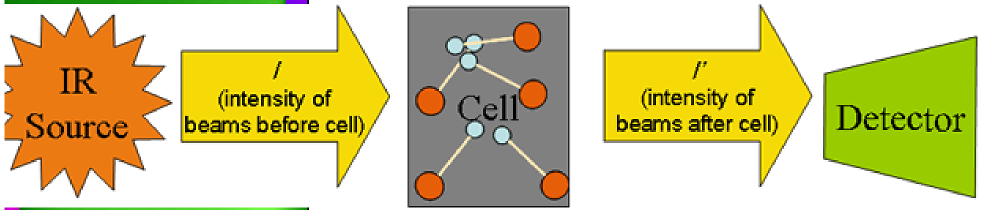
Bending (Wagging)



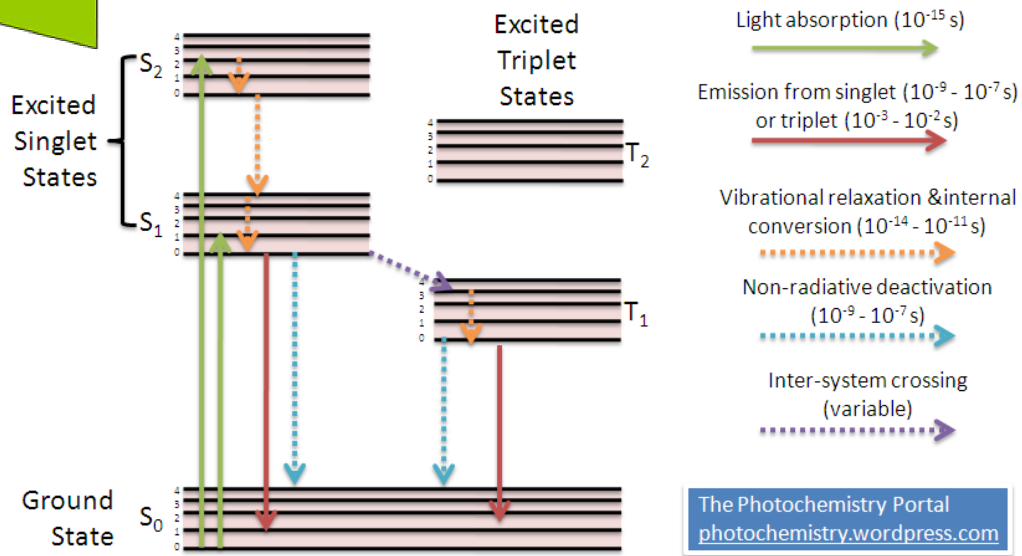
Bending (Scissoring)

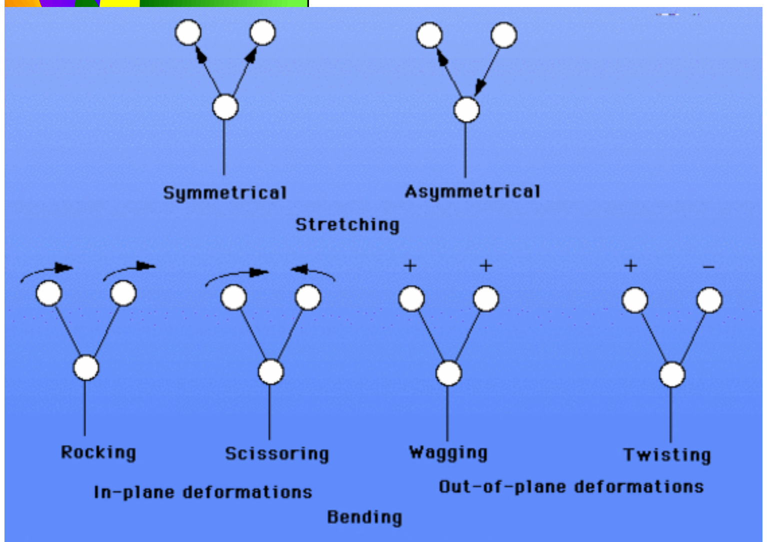
from chemwiki.ucdavis.edu

IR spectroscopy



www.kdijpn.co.jp

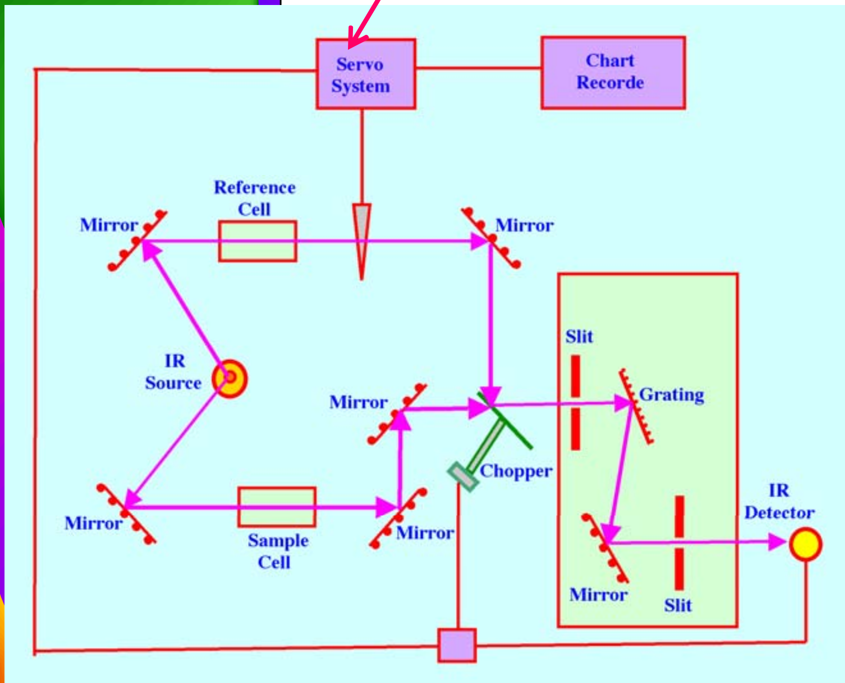


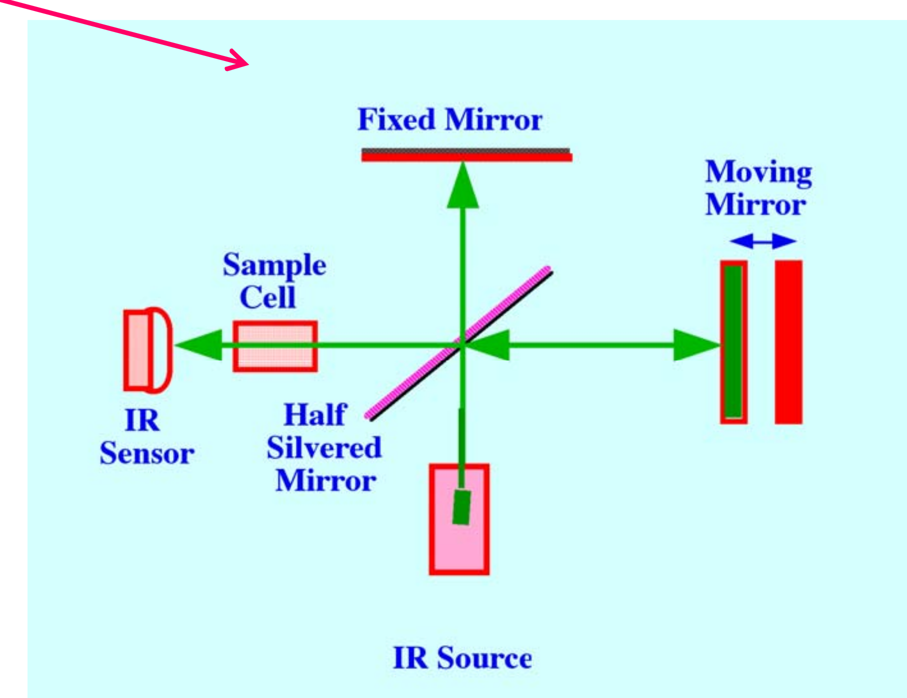


www.schodor.org

- IR radiation passes through a sample, some of it is absorbed, some of it is transmitted
- Spectrum represents the molecular absorption (transmission) creating a molecular fingerprint of the sample
- Useful for several types of analysis

Dispersion vs. FTIR spectrometer

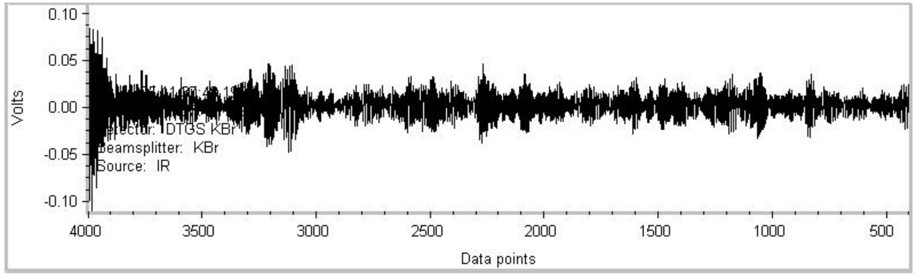




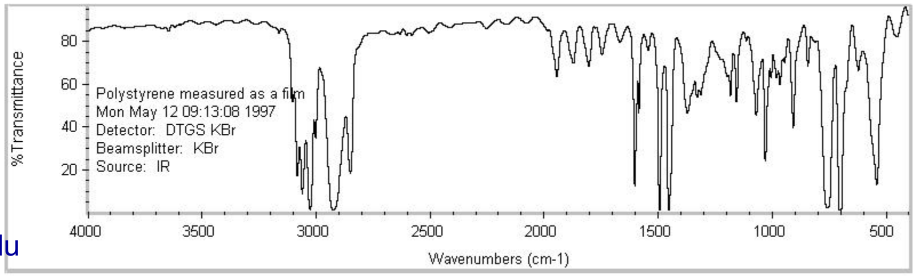
Raymond P. W. Scott
www.analyticalspectroscopy.net

FT-IR = Fourier Transform Infrared Spectroscopy

An interferogram



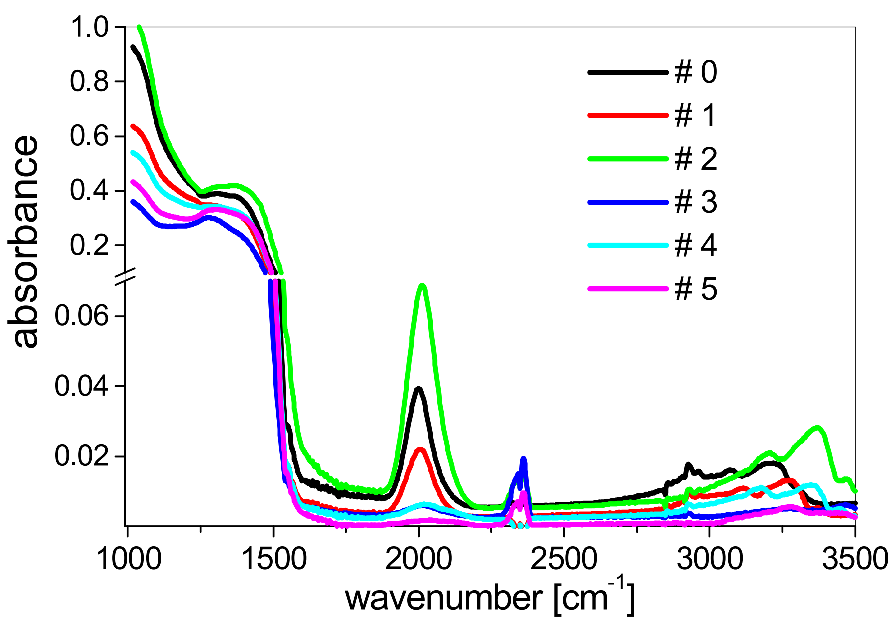
A spectrum

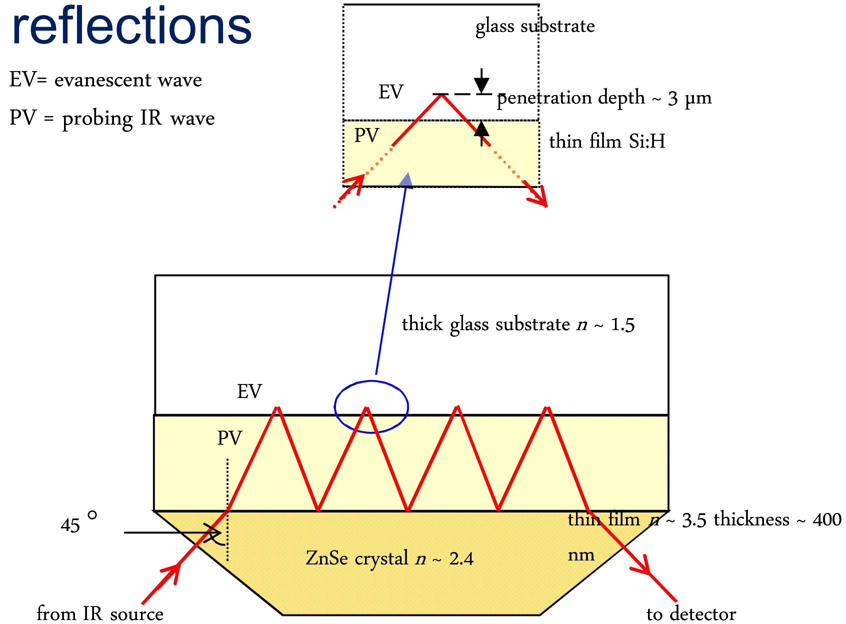


http://chemistry.oregonstate.edu

Attenuated total reflection

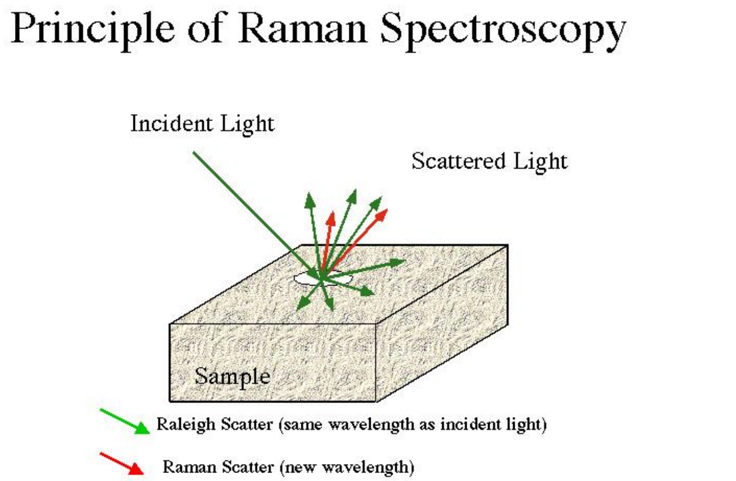
Enhanced sensitivity by
multipassing and/or multiple reflections





Internal mode - ATR (attenuated total reflection)
HATR (horizontal ATR) in multi-bounce sampling geometry,
ZnSe crystal with a bevelled edge of 45º
Spectral absorbance A = log(1/T)

Raman spectroscopy

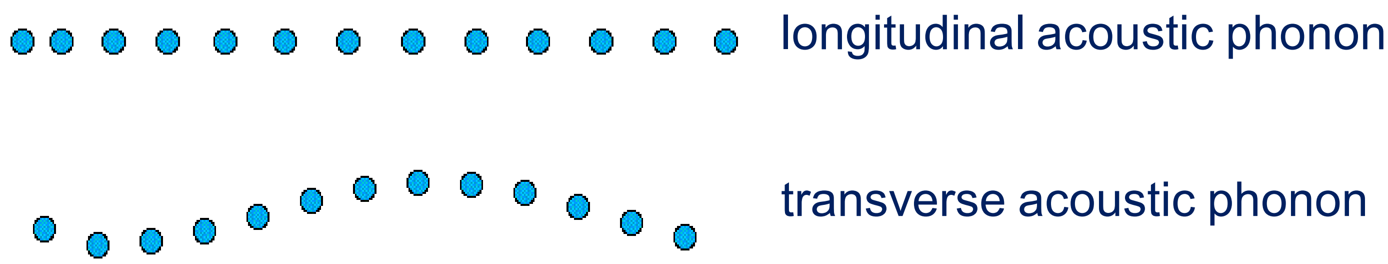


Alexander Couzis: www-che.engr.ccny.cuny.edu

Sir Chandrasekhara Venkata Raman
(1888 - 1970)
Nobel Prize 1930 for his work on "*the scattering of light and for the discovery of the effect named after him*"
(C. V. Raman and K. S. Krishnan: *A New Type of Secondary Radiation*, Nature, 121(3048), 501, 31 March 1928)

- Spatial charge separation under influence of electric field $\boldsymbol{E}$ induced dipole moment $\boldsymbol{\mu} = \alpha \boldsymbol{E}$
  α polarizability
- Raman effect small but accessible by use of lasers
- Complementary information to IR spectrosc.

Raman spectroscopy



There are two possible modes of vibrations of atoms in the crystal: **longitudinal** and **transverse**

In case of longitudinal mode the displacement of atoms from their equilibrium position coincides with the propagation direction of the wave, whereas for transverse mode, atoms move perpendicular to the propagation of the wave.

---

http://www.chembio.uoguelph.ca/educmat/chm729

- homonuclear diatomic molecules, low frequency range
- In situ analysis of organic and inorganic compounds
- Analysis of aqueous solutions and solids (powders)

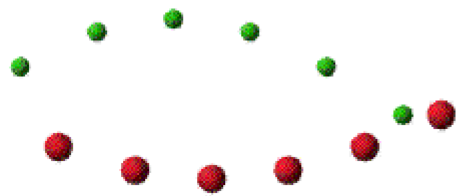
Raman spectroscopy

For one atom per unit cell the phonon dispersion curves are represented only by **acoustical** branches. However, if we have more than one atom in the unit cell **optical** branches will appear additionally.

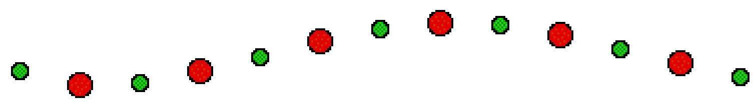
The difference between acoustical and optical branches arises because of the more options of vibrations for atoms in the unit cell.

For example, atoms A and B of diatomic cell can move together in phase (acoustical branch) or out of phase (optical branch)
Generally, for N atoms per unit cell there will be 3 acoustical branches (1 longitudinal and 2 transverse) and 3N-3 optical branches (N-1 longitudinal and 2N-2 transverse)

Diatomic chain:



transverse optical mode

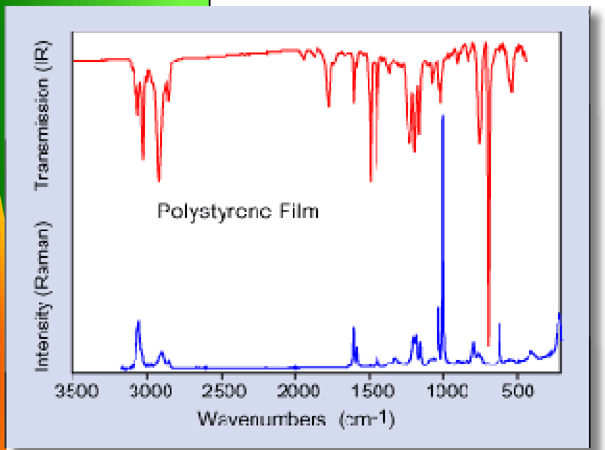


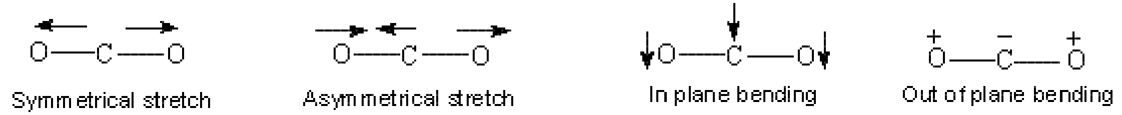
transverse acoustic mode

http://www.chembio.uoguelph.ca/educmat/chm729

Raman vs. IR spectroscopy

	Infrared	Raman
Physical effect	**Absorption** **Changing of the dipol moment** **(strong: ionic bondings like O-H,N-H)**	**Scattering** **Changing of the polarisability** **(strong: covalent bondings like C=C,C-S,S-S)**
Sample preparation	Optimal thickness (transmission mode) or sample contact (ATR) mode necessary	No contact, no destruction, simple preparation (if only); water as solvent or glass as container do not disturb the measurement
Problems	Strong absorption of glass, water, CO_2	Fluorescence
Materials	Mainly organic compounds	Nearly unlimited
Resolution: **- lateral** **- confocal**	 10 - 20 µm not possible	 1 - 2 µm ca. 2.5 µm
Chemical imaging	Mapping	Mapping and global imaging
Frequency range	4000 - 700 cm^{-1}	4000 - 50 cm^{-1} (Stokes and Antistokes)
Cost	Comparatively less expensive	Comparatively higher





No change in dipole moment therefore IR inactive
There is change in polarisability therefore Raman active

There is change in dipole moment therefore IR active but Raman inactive

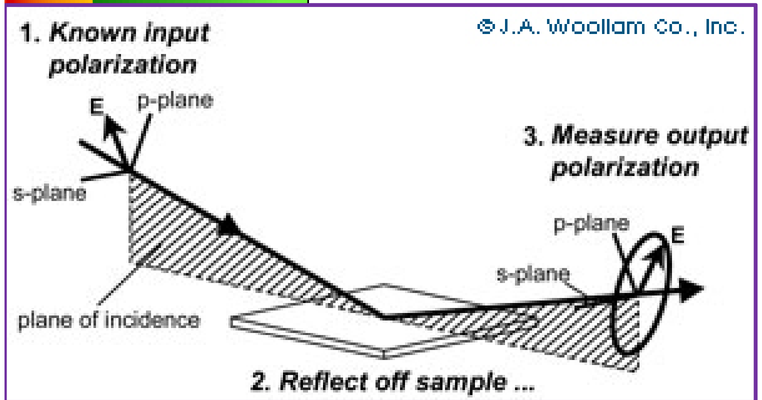
The deformation vibrations of CO_2 are degenerate and appear at the same region (666 cm^{-1}) in the IR spectrum of CO_2. There is no change in polarisability therefore these vibrations are Raman inactive.

www.chemvista.org

www.inphotonics.com

Ellipsometry

- measures changes in **polarization of light** reflected off or transmitted through a material structure, mostly thin films or thin film structures
- is applied to characterize the film thickness (esp. in nanometer scale) and optical parameters of material (connected with microstructure) … **depend on the model**
- The polarization change is represented by **ellipsometric parameters *ψ*** (amplitude ratio) **and *Δ*** (the phase difference between s- and p-polarized wave before and after reflection)
- *Ψ, Δ* depend on optical properties and the thickness of individual layers



Fundamental ellipsometric equations:

Complex reflectance ratio $\rho = \frac{r_p}{r_s}$

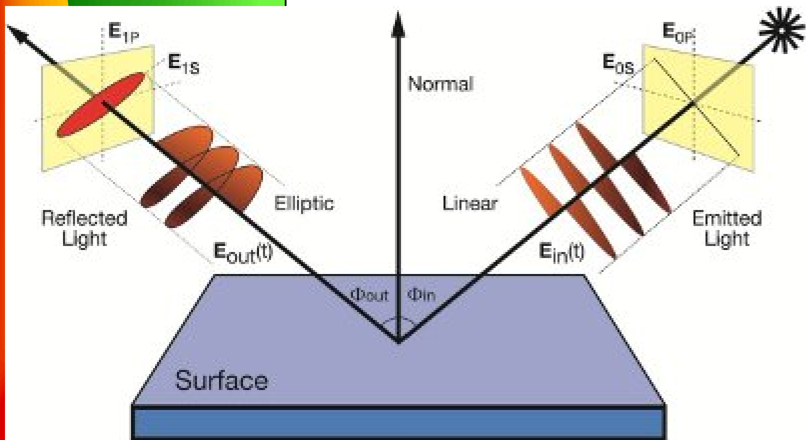
$\rho = \tan\psi e^{j\Delta}$ $\tan\psi e^{j\Delta} = \frac{r_p}{r_s}$

reflectance $R_p = |r_p|^2$ $R_s = |r_s|^2$

www.jawollam.com

Data from ellipsometry

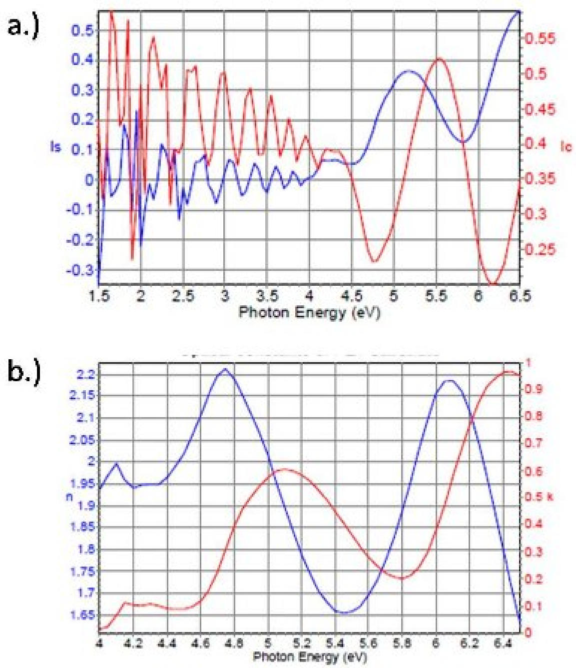
- Measuring spectra of *ψ and Δ*
- Ellipsometry at fixed angle, ellipsometry at fixed wavelength, spectral ellipsometry,
- More complex: variable angle spectral ellipsometry (VASE)
- Fitting experimental spectra; a model representing the structure must be created
- Extracting information on: film thickness, complex refractive index, surface roughness, interfacial regions, composition, crystallinity, homogeneity etc.



Raw data, e.g.:

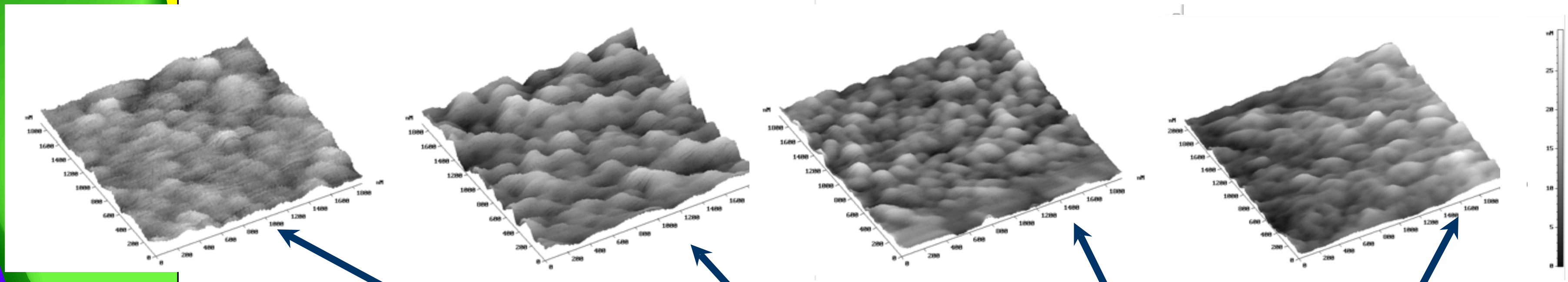
$$I_c = \sin 2\psi \cos\Delta$$

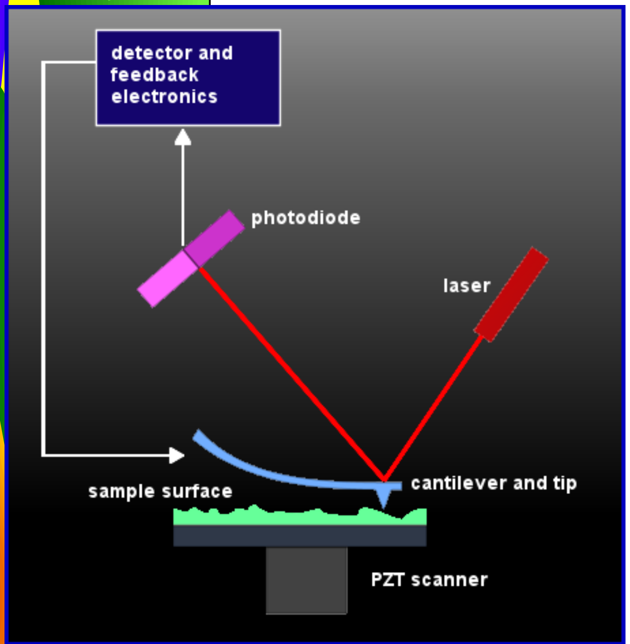
$$I_s = \sin 2\psi \sin\Delta$$

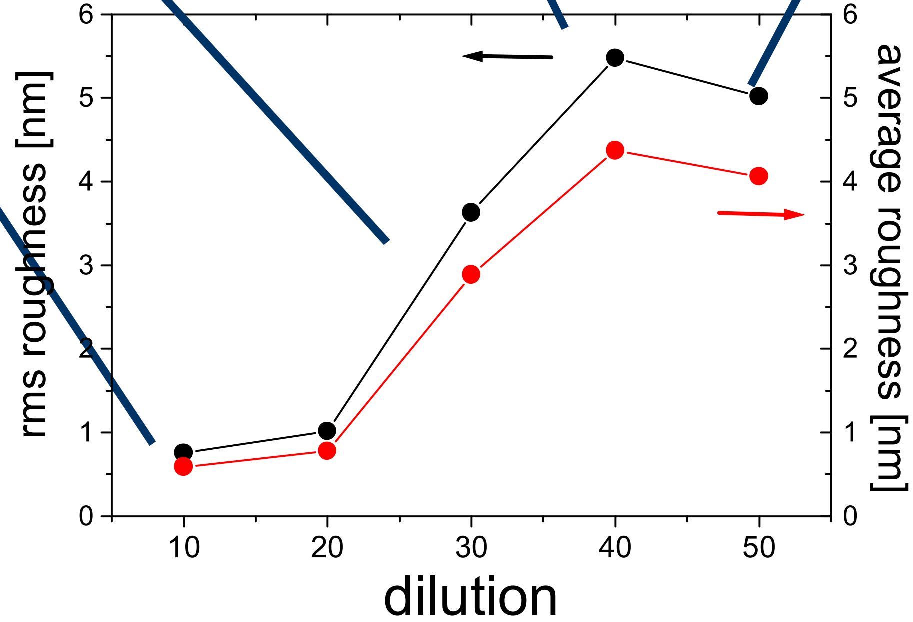


http://www.americanlaboratory.com

Surface morphology by AFM





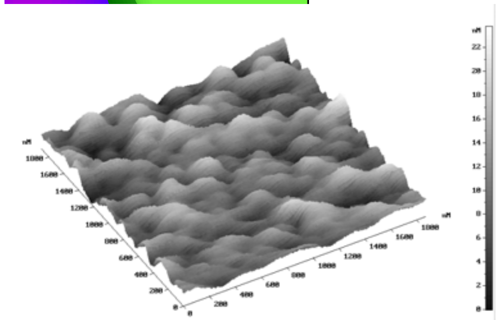


Surface roughness

… one of characteristics of surface finish (roughness, waviness, lay)

… is defined as the deviation of the actual surface topography from the mean line

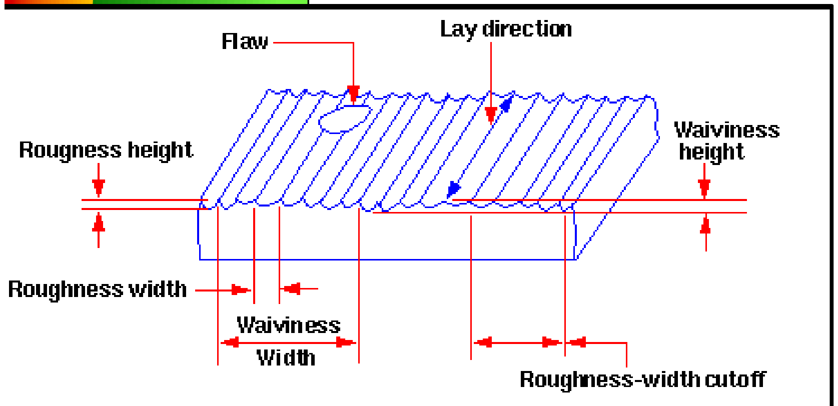
… a range of vertical amplitude parameters reported to describe the surface roughness, many related to surface statistics:



Peak-to-valley roughness (maximum height profile):

$$R_{pv} = Z_{max} - Z_{min}$$

Average roughness (arithmetic): $R_{av} = \sum_{i=1}^{N} \frac{|Z_i - \bar{Z}|}{N}$



Surface characteristics (Courtesy, ANSI B46.1 - 1962)

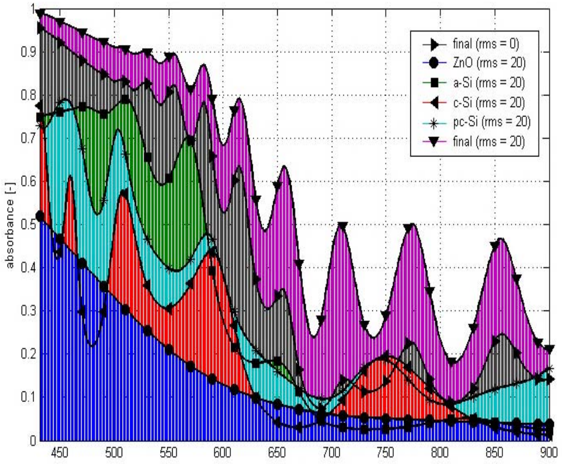
RMS roughness: $R_{RMS} = \sqrt{\sum_{i=1}^{N} \frac{(Z_i - \bar{Z})^2}{N}}$

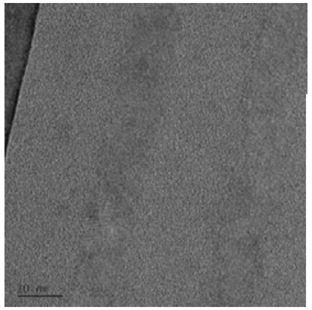
… other parameters - slope, spacing and counting (characterizing surface texture)

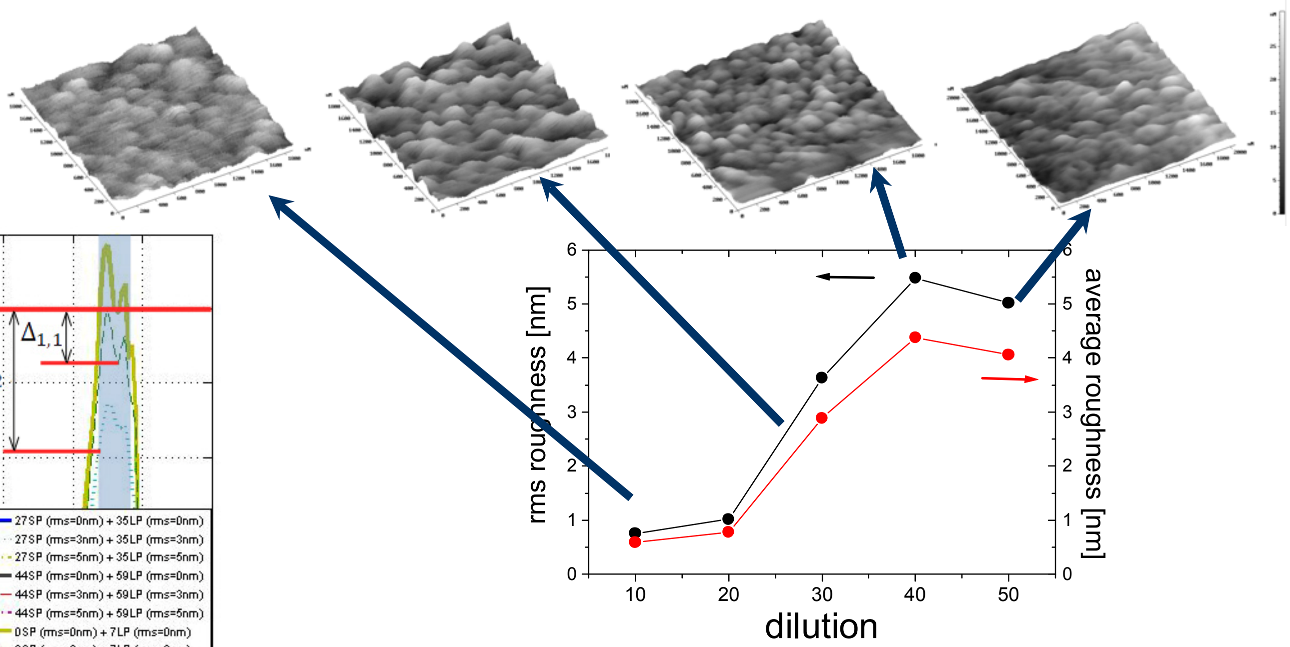
Surface and interface roughness

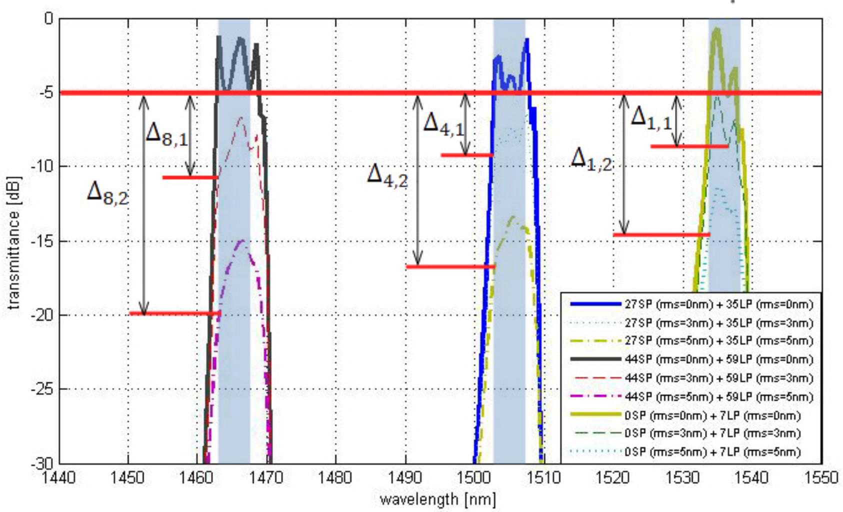
Pros & Cons of a rough surface:

- Solar cells – more effective photon harvesting (+ also other technologies)
- Band-pass filters on **a-Si/SiO_2** e.g. for optical access technologies– degradation of transfer functions









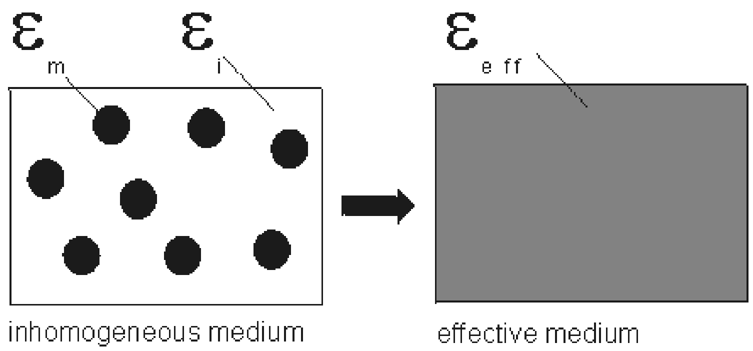
Müllerová, J. et al.: Acta Phys. Slov. vol. 55, No.3, 351 – 359, 2005

Effective medium approximation (EMA)

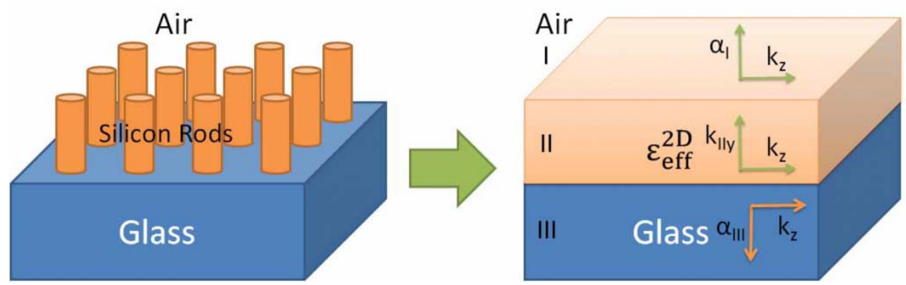
EMA - treatment of **macroscopically inhomogeneous medium** – quantities such as the conductivity, dielectric function, elastic modulus etc. vary in space: e.g.

- Metal-dielectric composites
- Porous material, e.g. rocks
- Polycrystalline samples of an anisotropic material
- Polycrystalline elastic material
- Photonic metamaterials

a composite system consisting of particles embedded in a host material

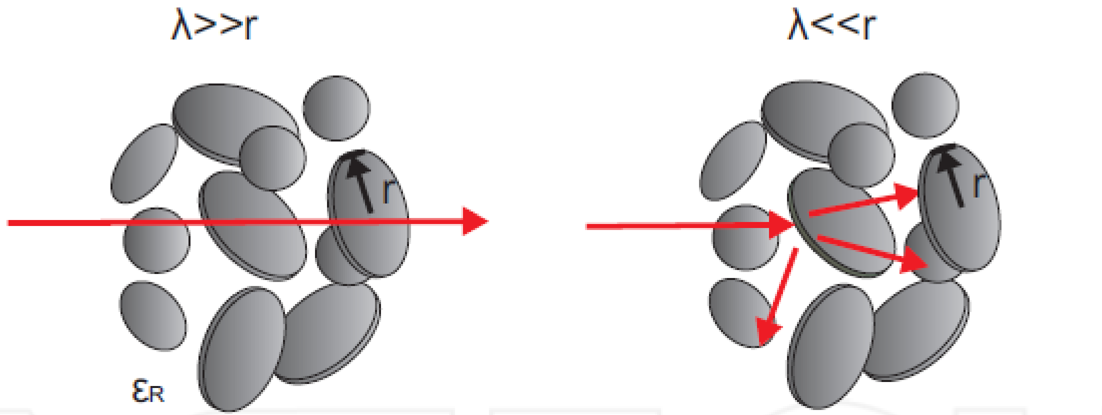


www.pi1.physik.uni-stuttgart.de

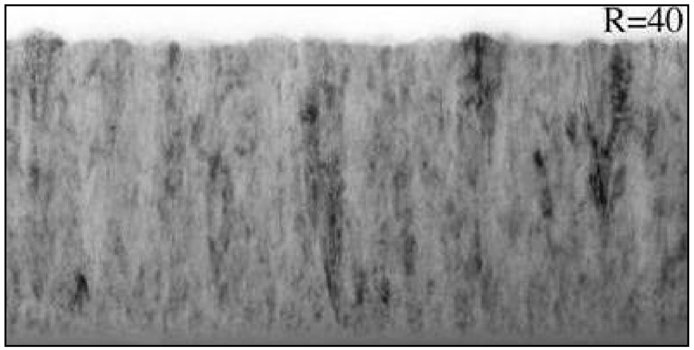


Hanhong Gao, Baile Zhang, Steven G. Johnson, and George Barbastathis, "Design of thin–film photonic metamaterial Lüneburg lens using analytical approach," Opt. Express **20**, 1617-1628 (2012)

Effective medium approximation (EMA)



If the particle size is much smaller than the wavelength of interest, scattering effect are negligible and a quasi-static model is sufficient, otherwise scattering has to be taken into account



Volume inhomogeneities (e.g. voids) or mixed-phase materials:

J. Müllerová et al., Appl. Surf. Sci 254,2008, pp. 3690-3695

M. Scheller, , Ch. Jansen, M. Koch In: Recent optical and photonic technologies, Ed. Ki Young Kim, INTECH, 2010

Effective medium approximation (EMA)

complex refractive indices of effective medium (eff), and materials (1,2) in the host medium (h) of volume fractions *p* (1,2)

$$p_1 \frac{\hat{n}_1^2 - \hat{n}_h^2}{n_1^2 + 2n_h^2} + p_2 \frac{\hat{n}_2^2 - \hat{n}_h^2}{\hat{n}_2^2 + 2\hat{n}_h^2} = \frac{\hat{n}_{eff}^2 - \hat{n}_h^2}{\hat{n}_{eff}^2 + 2\hat{n}_h^2}$$

Lorentz-Lorenz (1870) - host medium is vacuum
Maxwell Garnett (1904)- host medium is one of 1,2
Brugemann (1935, BEMA) – host medium is effective medium

BEMA – complex dielectric function of a composite film of *i* constituents with their own dielectric functions and volume fractions p_i

$$\hat{n}_i = \sqrt{\hat{\varepsilon}_i}$$

$$\sum_i p_i \frac{\varepsilon_i - \varepsilon_{eff}}{\varepsilon_i + 2\varepsilon_{eff}} = 0 \ , \ \sum_i p_i = 1$$

Outline

1. Introduction
2. Motivation
3. Thin films
4. Measurement techniques
5. **Photonics materials:**
   - **overview**
   - **dielectrics**
   - **group IV element based photonic materials: Si**
   - **organic materials**

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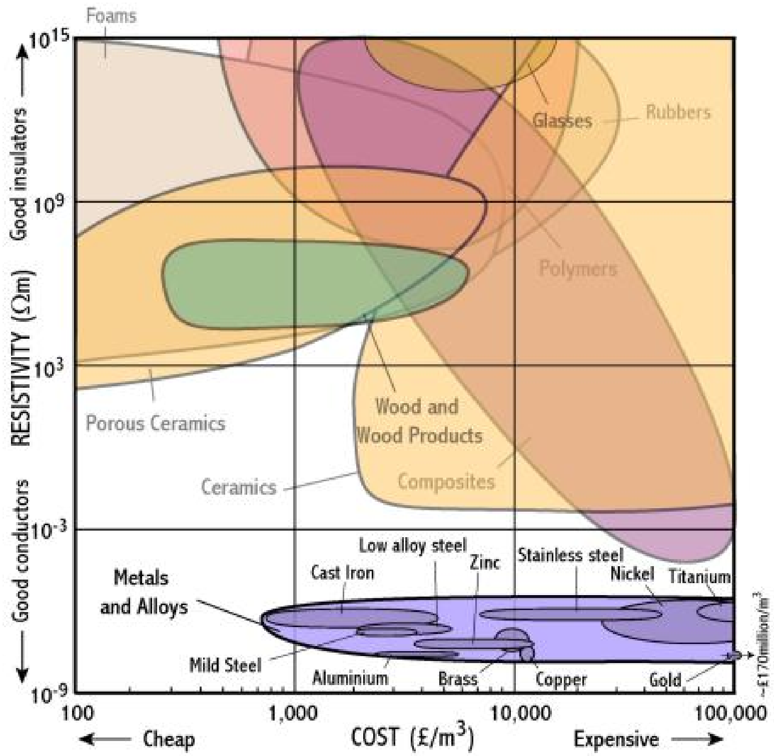
Material properties

Usually - a material property is:

1. some quantifiable behaviour of a material, e.g. acoustic, electrical, optical, thermal, chemical …
2. characteristic of the material, not of the configuration in which it exists or is used

However:

The second issue is vitally important for applications – therefore it can be seen as material property in a specific configuration



Photonics materials:
Optical properties matter = reflectivity, absorbance, luminosity, color, refractive index …

www-materials.eng.cam.ac.uk

Overview of photonics materials

According to conductivity:
1. Metals
2. Semiconductors
3. Dielectrics

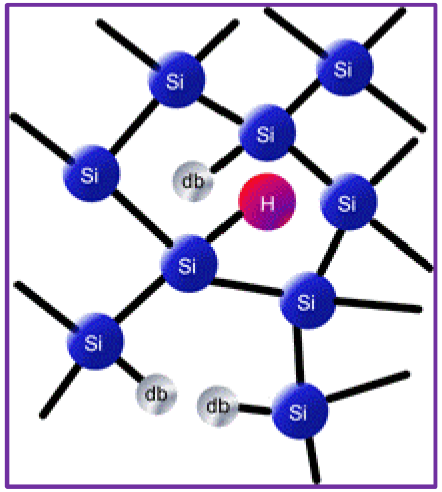
According to microstructure:
1. Composites
2. Multiphase materials
3. Metamaterials

According to structure:
1. Crystalline
2. Amorphous
3. Glasses

Density:
1. Metals
2. Ceramics, porous ceramics
3. Foams

Response to Radiation:
1. Linear
2. Nonlinear

a-Si:H



Christoph Boehme, PhD , University of Utah

Corning Eagle XG ®
glass substrate

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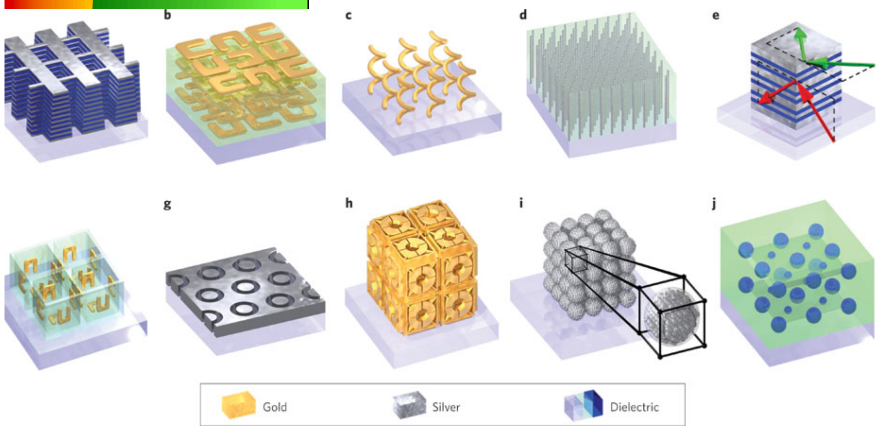
Dielectrics and photonics

- insulators, a low electrical conductivity, a high polarizability (related to the relative permittivity), can be solids, liquids, gases
- refractive index of non-magnetic material: $n = \sqrt{\varepsilon_r}$
- In photonic: mainly solids (amorphous and crystalline)
- **mostly used – oxides, e.g. SiO_2 (silica), sulphides, polymers**

Oxides as low-k dielectrics and high-k dielectrics: ε_r related to SiO_2 ($\varepsilon = 3.9$)

- Low-k: fluorine-doped SiO_2, carbon-doped SiO_2, porous SiO_2
- High-k: (used as gate oxides in semiconductor devices to avoid leakage currents instead of using SiO_2 gates < 2 nm) – Hf (Ta, Sr, Ti)-based compounds, e.g. HfO_2 ($\varepsilon = 25$), $HfSiO_4$ ($\varepsilon = 11$), $SrTiO_3$ ($\varepsilon = 2000$), TiO_2 ($\varepsilon = 80$)



Nature Photonics, 5,523,2011

Applications in photonics: optical fibers, coatings, substrates, sensors, filters etc.

Special representatives: Metallo-dielectrics for metamaterials and photonic crystals – metal islands of various symmetry embedded in dielectric media

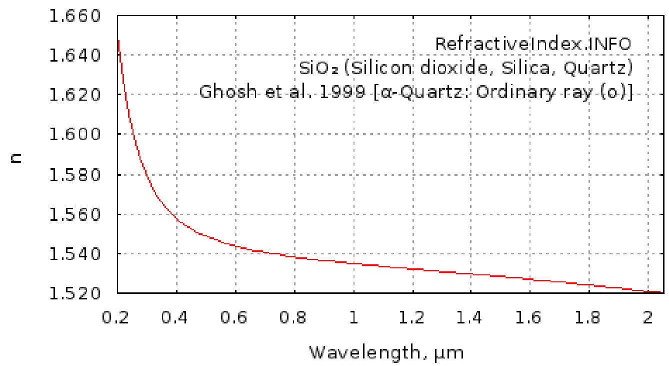
Optical glasses

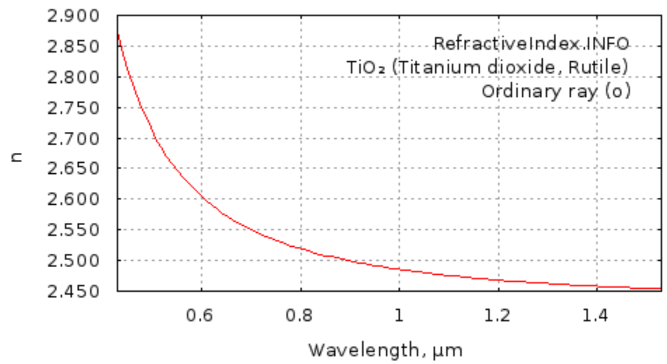
- **Crown glasses** = a soda-lime-silica composite, containing silicon dioxide (silica), Na_2O (soda), and CaO (lime) (95% of glasses), typical refractive index 1.5 – 1.6
- **Flint glasses** contain 45-65% lead oxide - they are high-density, high-dispersion, high-refractive-index (~1.7) glasses. Lanthanum and other rare earths are used to make flint glasses
- **Barium glasses** containing barium oxide rather than lead oxide; refractive indices comparable to the flints, but have lower dispersions
- other additives, so-called **"glass formers"** such as boron oxide (B_2O_5), phosphorus pentoxide (P_2O_5), germanium oxide (GeO_2) can be used.

Photonics oxides

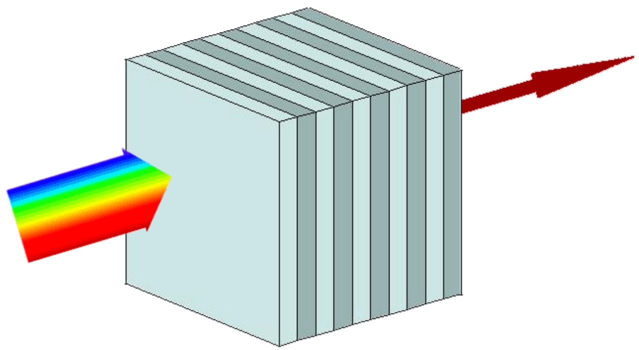
Applications: optical coatings, CMOS technologies (as for photonics, e.g. MOS solar cells), substrates, nanocomposites, multilayer structures, e.g. spectral filters, gratings, modulators, integrated photonic devices, optical sensors, fuel cells

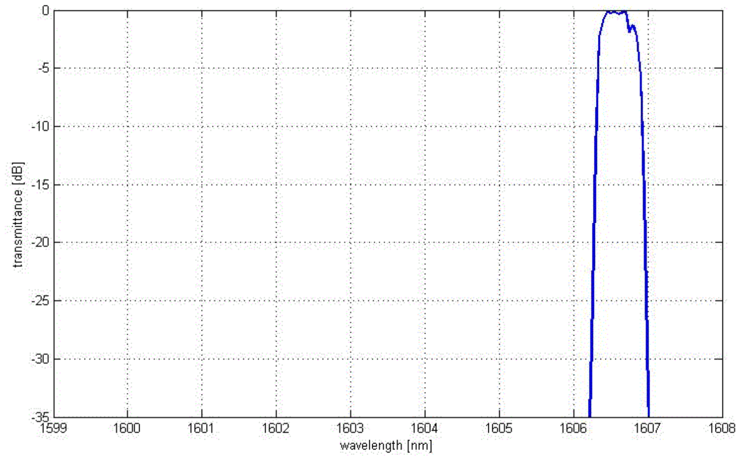
Excellent transparency from the UV to the IR





www.refractibeindex.info





By courtesy of L. Scholtz, IAS

Metal oxides for photonics

- provide a means of tailoring the band gap
- cheap and abundant, versatile, environmental stable
- battery storage, fuel cells, touchscreen technology and all types of computer switches, LC displays
- mostly oxides of transition metals, often complex e.g. doped or co-doped: ZnO, ZnO:Al (AZO), ZnO:Ga (GZO), SnO_2, Y_2O_3, ITO (In_2O_3 + SnO_2)
- some of them are ferroelectrics (e.g. perovskites such as $BaTiO_3$, Pb(Zr, Ti)O_3)

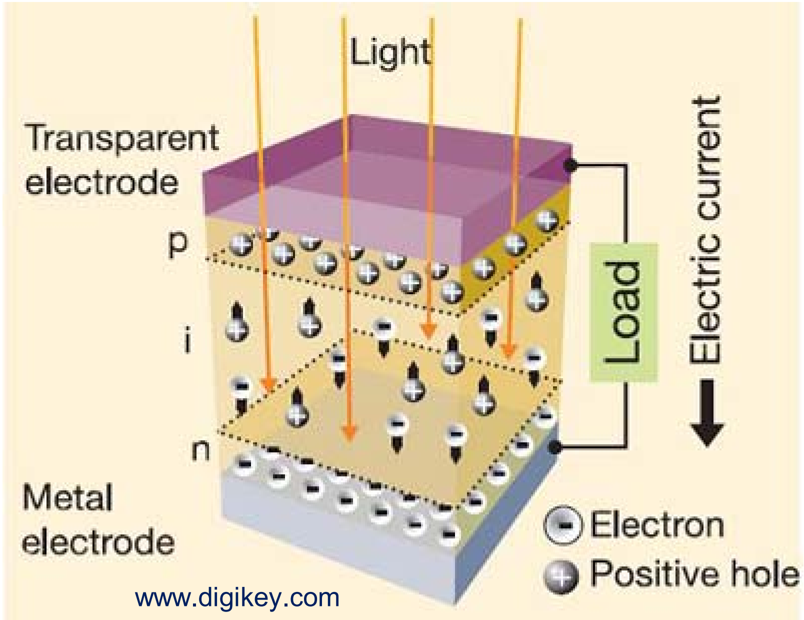
… and a piece of photonics/non-photonics apps: ITO ice- and fog-free windshields (window defrosters)

www.autoevolution.com

Metal oxides special: transparent and conducting

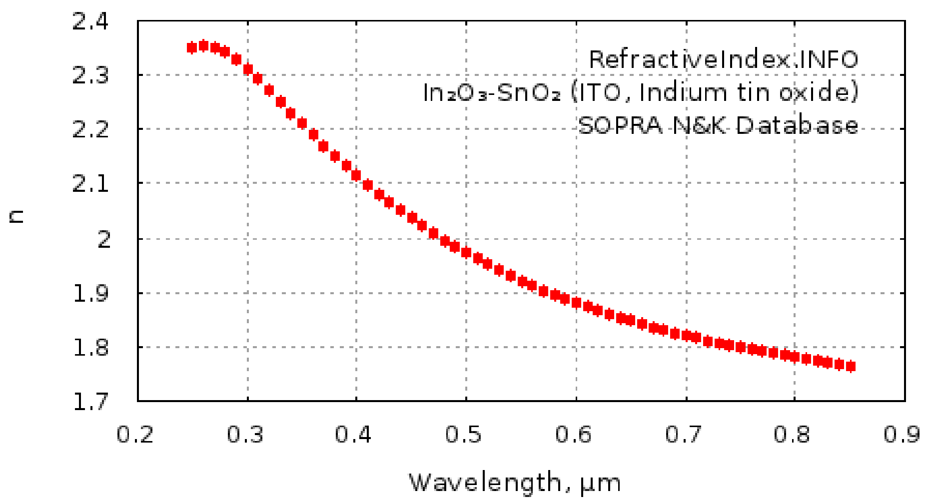
- remarkable **coexistence of electrical conductivity and optical transparency**
- low emissivity- electrochromic windows, heat barrier coatings
- transparent electrodes for solar cells or flat screen HDTVs, smart displayes, window defroster, transparent TFF, LED …
- **a wide band gap > 3 eV**
- resistivity < 10^{-4} Ω·cm, extinction coefficient in Vis ~ 10^{-4}
- transparency – depends on the atomic arrangements of metal ions in oxide structures, intrinsic or intentionally introduced defects etc.
- polycrystalline or amorphous; quite exotic physics, but engineering the band gap possible
- binary or ternary compounds, often complex, most n-type, rarely p-type semiconductors (ZnO:Mg, ZnO:N, ZnO:In, NiO)
- ZnO, ZnO:Al (AZO), ZnO:Ga (GZO),, SnO_2, Y_2O_3, ITO (In_2O_3 + SnO_2= $In_xSn_{1-x}O_2$)

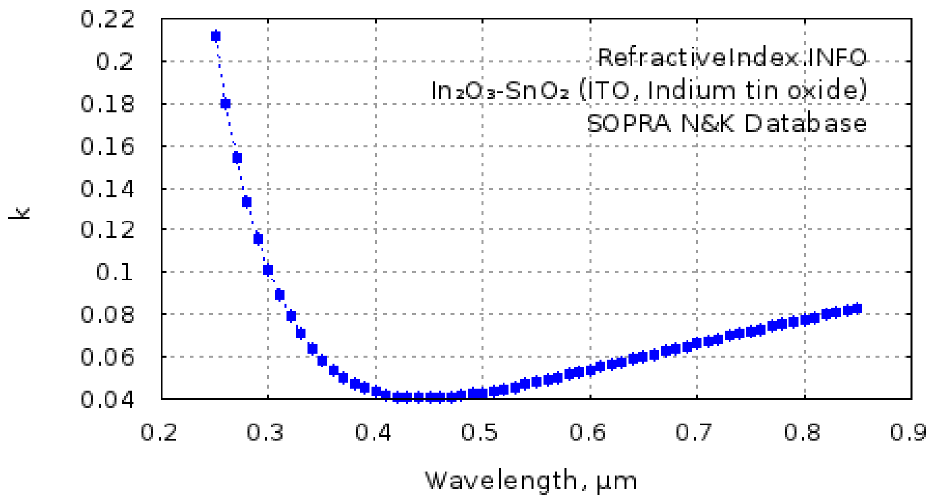
TCO in photovoltaics

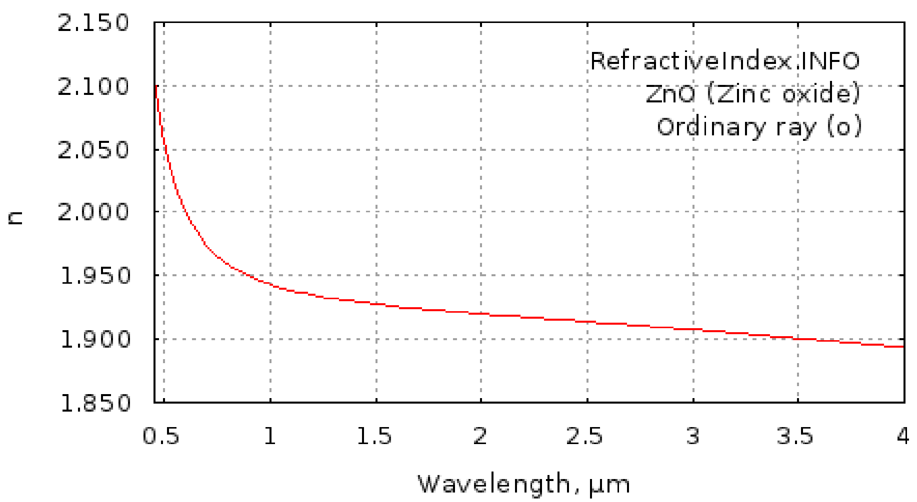


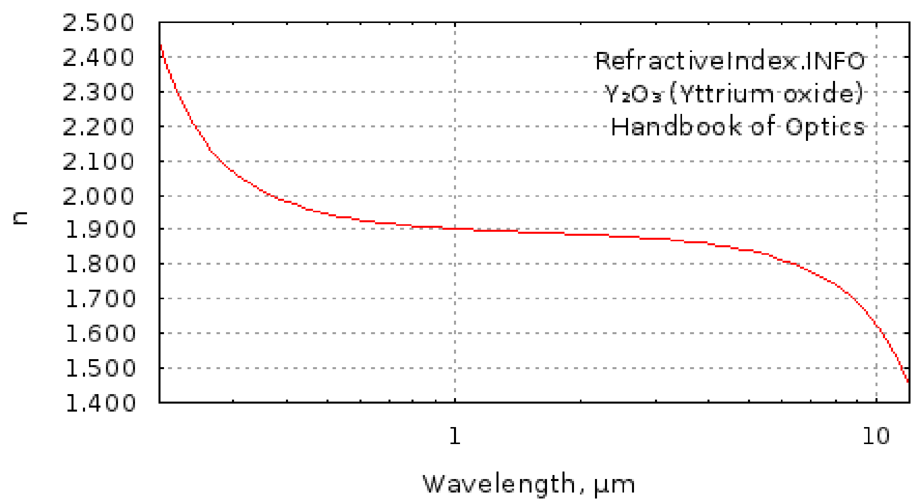
PV conversion = photoelectric effect based on the separation of hole and electron pairs when exposed to light

TCO optical properties







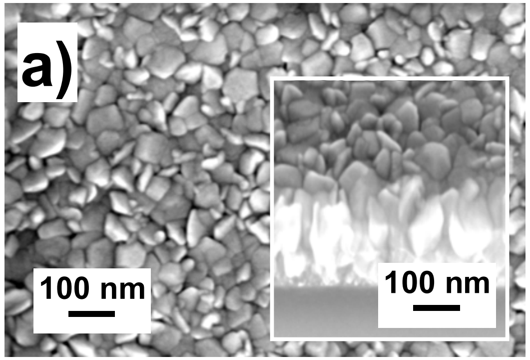


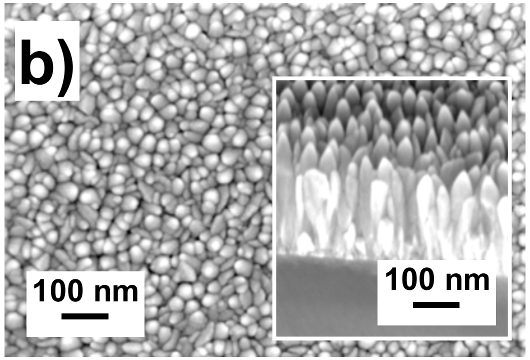
Transparent conducting oxides

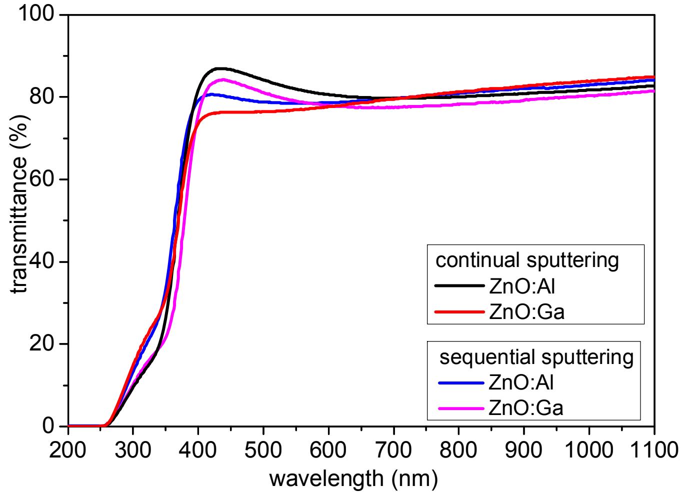
General knowledge - optical properties depend on structure

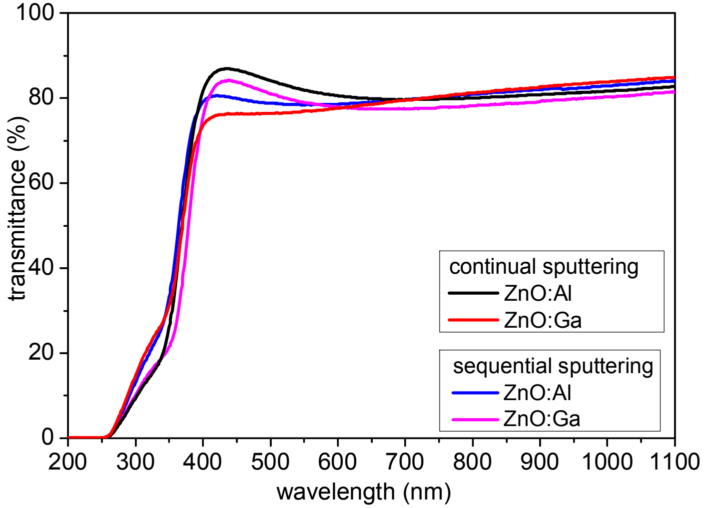
Structure evolution by the deposition and post-deposition processes

Fresh results on AZO, GZO deposited by sequential or continual sputtering

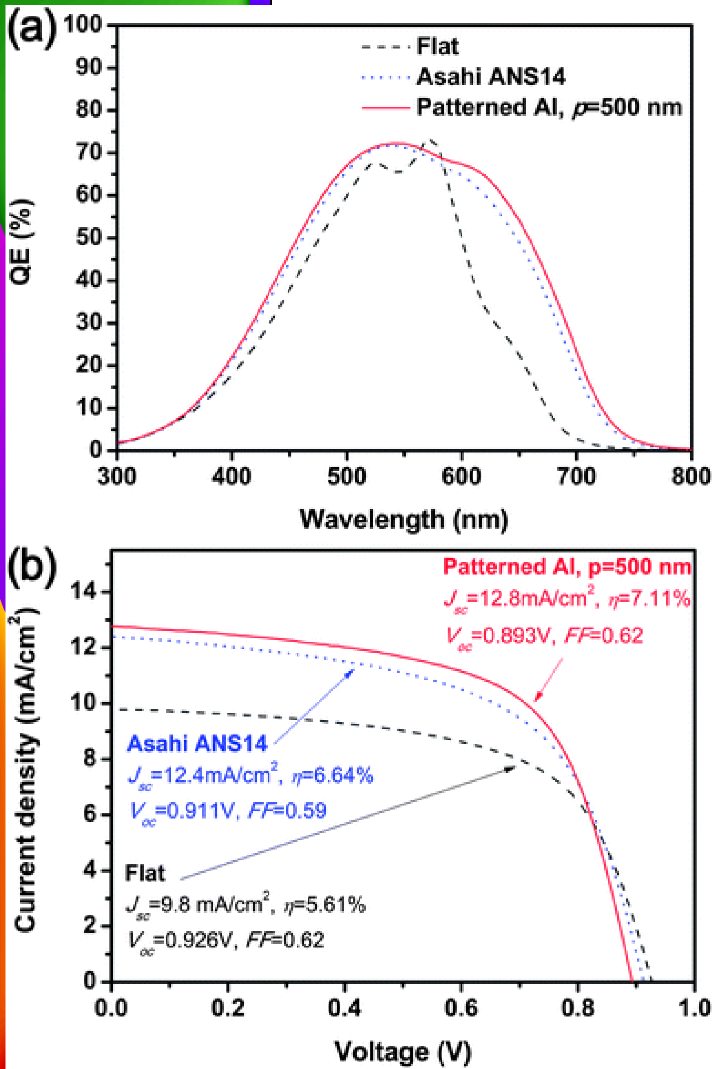




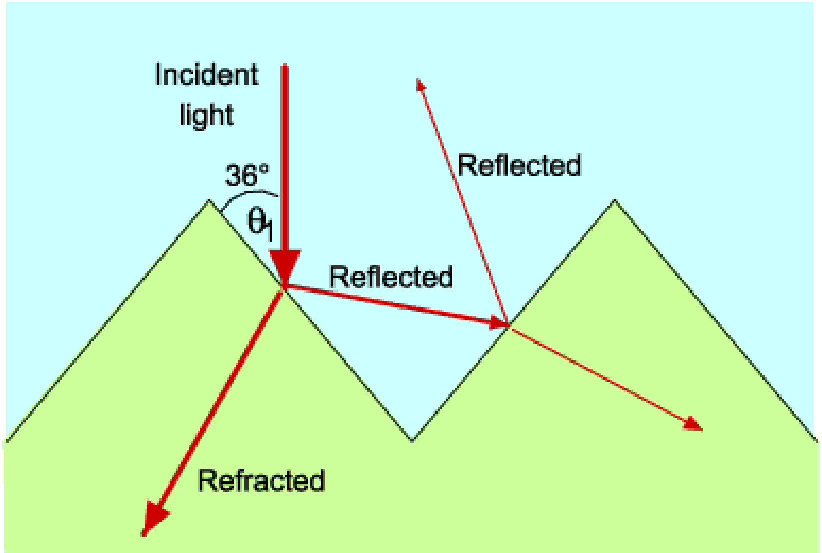




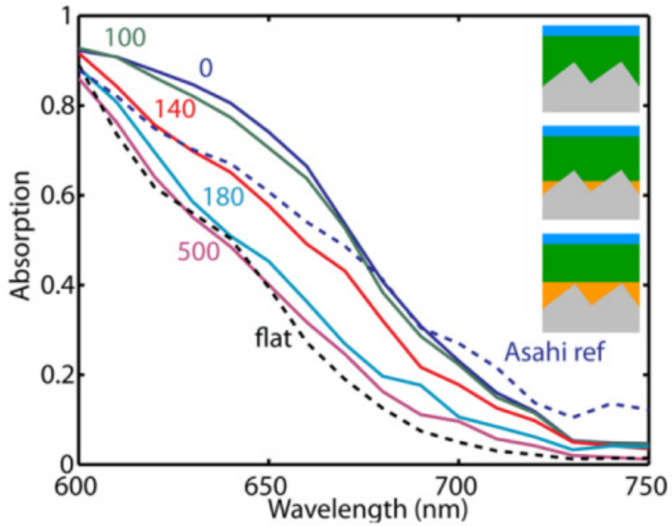
Patterned surfaces: light trapping



H. Huang et al.: Energy Environ. Sci., 6, 2013, 2965



A textured silicon solar cell: www.pveducation.org



M. van Lare, F. Lenzmann, A. Polman: Optics Express, 21, 2013, 20738

Nonlinear photonics materials

Nonlinear optics - under certain circumstances the linear superposition principle with the interaction of light and matter is violated

Material polarization:

$$\vec{P} = \overrightarrow{P}(\vec{E}) = \vec{P}^{L} + \vec{P}^{NL} = \varepsilon_0 \chi \vec{E} + \varepsilon_0 \chi^{(2)} \vec{E}^2 + \varepsilon_0 \chi^{(3)} \vec{E}^3 + \cdots$$

Second order phenomena (Pockels effect, SHG) $P^{NL} = \varepsilon_0 \chi^{(2)} E^2$

Third order phenomena (THG ,Kerr effects) $P^{NL} = \varepsilon_0 \chi^{(3)} E^3$

Typical materials – dielectrics crystals and optical glasses

Second order materials: BBO, $LiNbO_3$, $LiIO_3$, KDP …

Third order materials: Al_2O_3, CdS, GaAs, LiF, … organic dyes

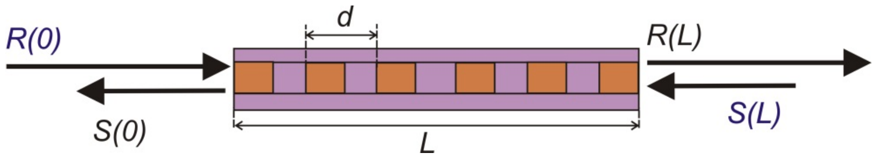
Applications– many photonic devices, e.g. switches, modulators …

In optical fibers – stimulated scattering, SPM, XPM, FWM, supercontinuum generation

Effective refractive index

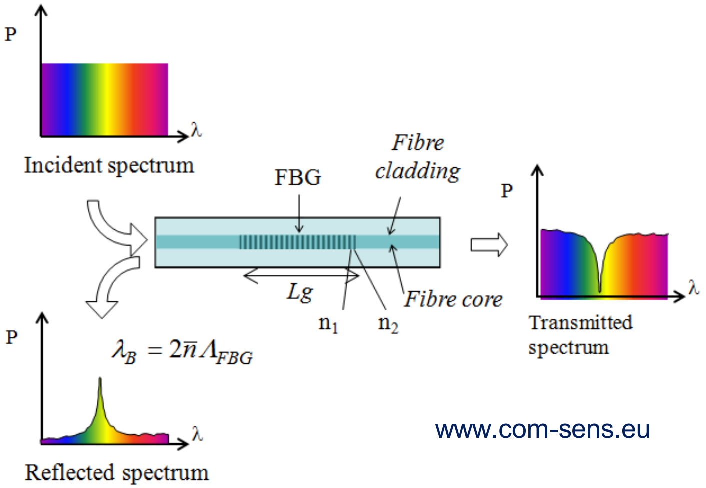
Linear Fiber Bragg gratings (FBG) – periodic alternation of segments of high and low refractive index along the optical fiber, various index profiles possible

Applications: fiber grating lasers, fiber grating sensors, WDM multi/demultiplexers, dispersion compensators ….



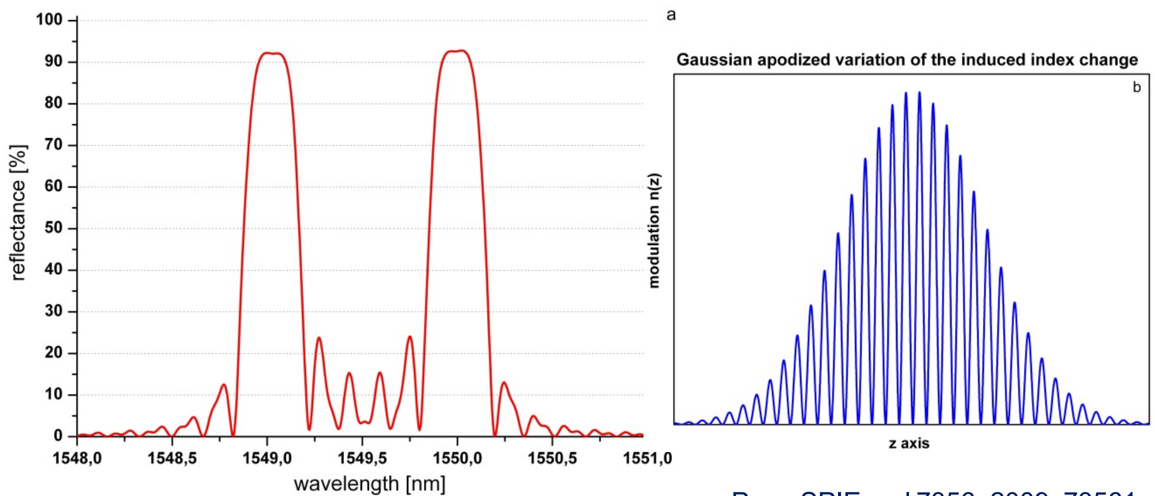
$$n(z) = n_{eff} + V_n g v\left(\cos\frac{2\pi z}{d}\right)$$

$$\lambda_{Bragg} = 2 \cdot n_{eff} \cdot d$$



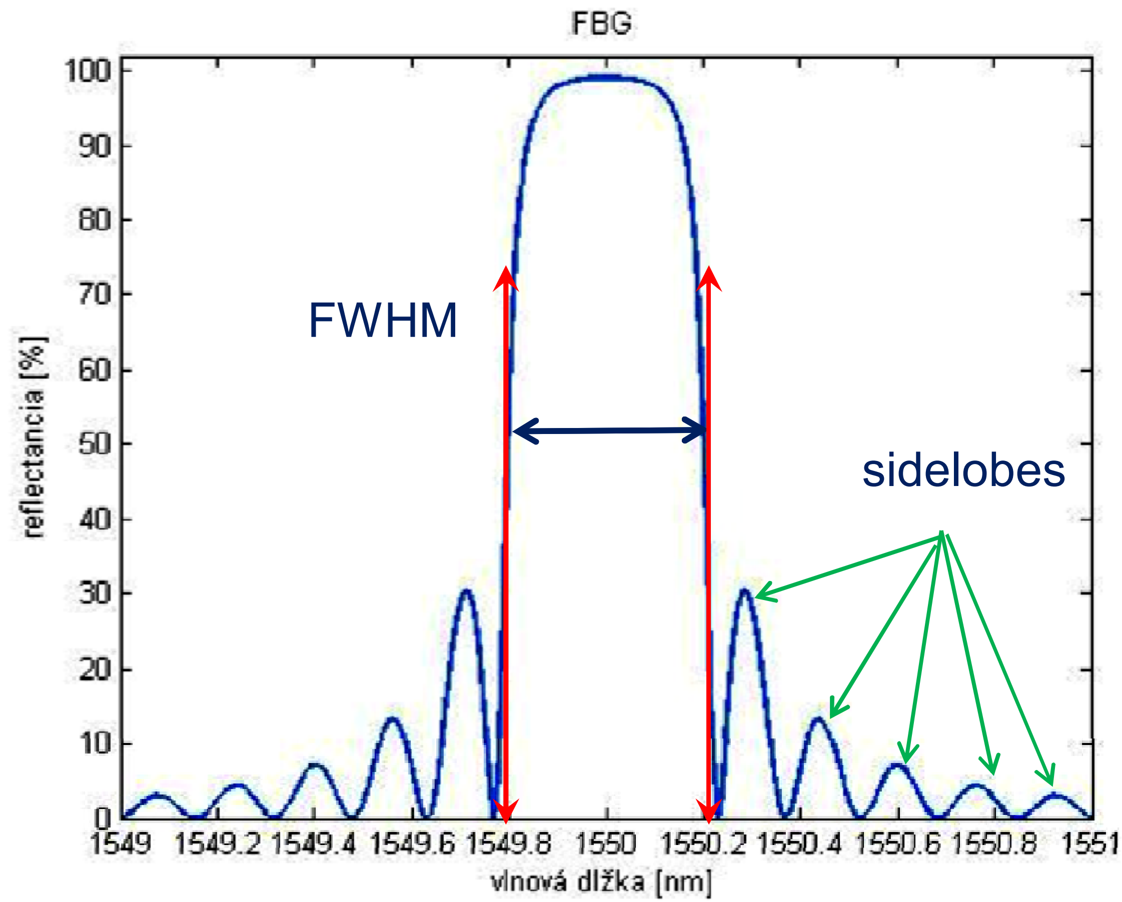
www.com-sens.eu

Two FGBs in a cascade – Gaussian apodization of the refractive index



E. Gemzicky, J. Müllerova, Proc. SPIE, vol 7356, 2009, 73561

FBG reflectance spectrum



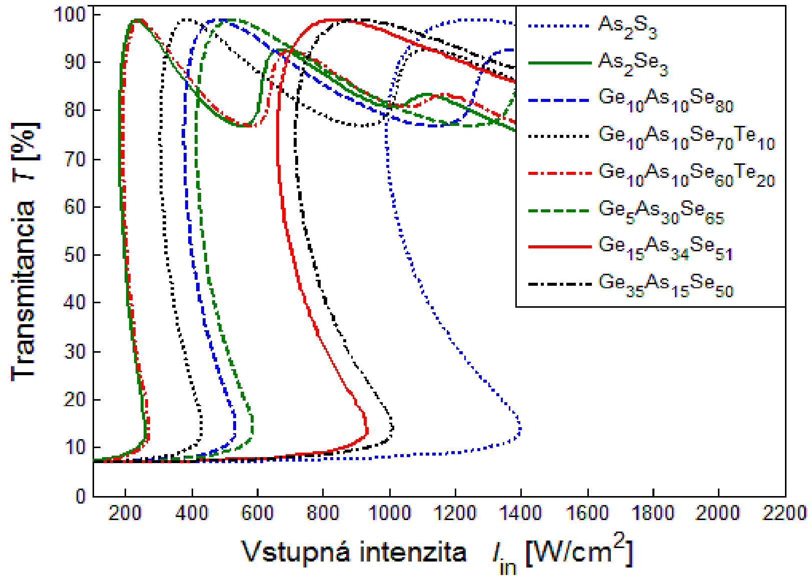
Chalcogenide glasses and FBGs

- Group VI elements: Se, S or Te
- Group IV and V elements: As, Ge, Sb
- High transparency in IR
- Quick non-linear response, high non-linear refractive index n_2

$$n = n_0 + n_2 \left|\vec{E}\right|^2$$

$$n(z) = n_{eff} + V_n g v\left(\cos\frac{2\pi z}{d}\right) + n_2\left|\vec{E}(z)\right|^2$$

Chalkogenide glass	n_{eff}	n_2 x10^{-14} [cm^2/W]
As_2S_3	2,45	2,6
As_2Se_3	2,81	14
$Ge_{10}As_{10}Se_{80}$	2,58	6,8
$Ge_{10}As_{10}Se_{70}Te_{10}$	2,74	8,4
$Ge_{10}As_{10}Se_{60}Te_{20}$	2,90	13,4
$Ge_5As_{30}Se_{65}$	2,72	6,2
$Ge_{15}As_{34}Se_{51}$	2,64	3,9
$Ge_{35}As_{15}Se_{50}$	2,63	3,6



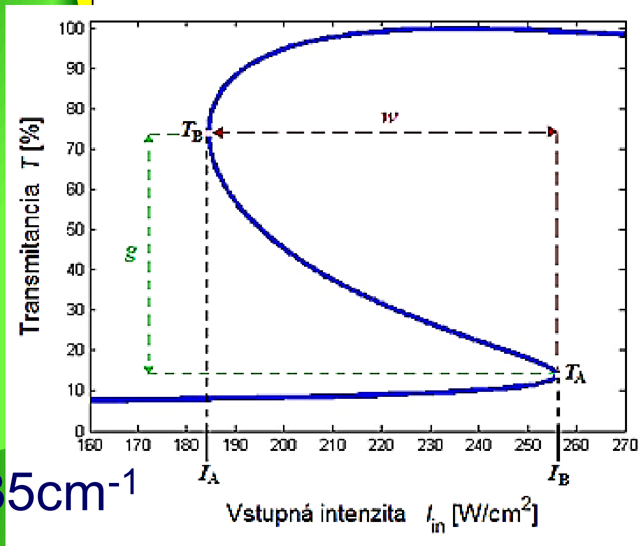
λ_{Bragg}=1550 nm, FBG parameters L=1 cm, V_n=0,0001

E. Jurisova, J. Mullerova, Communications 2, 2012, 5-10

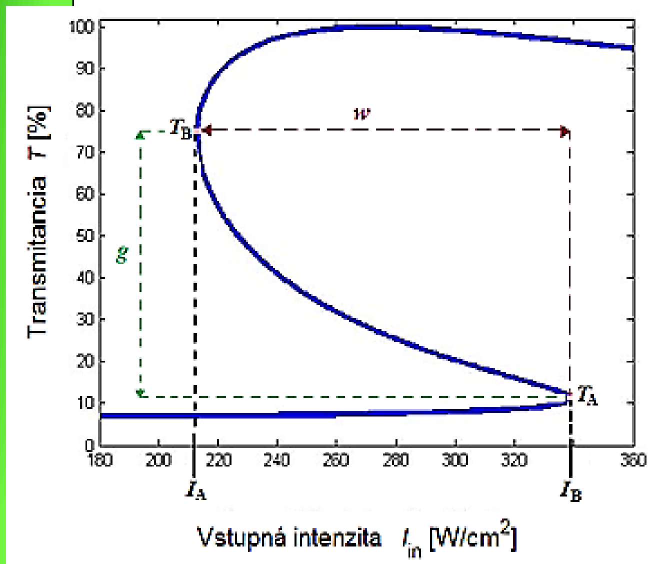
Chalcogenide nonlinear FBGs

As_2Se_3

$\delta=0$

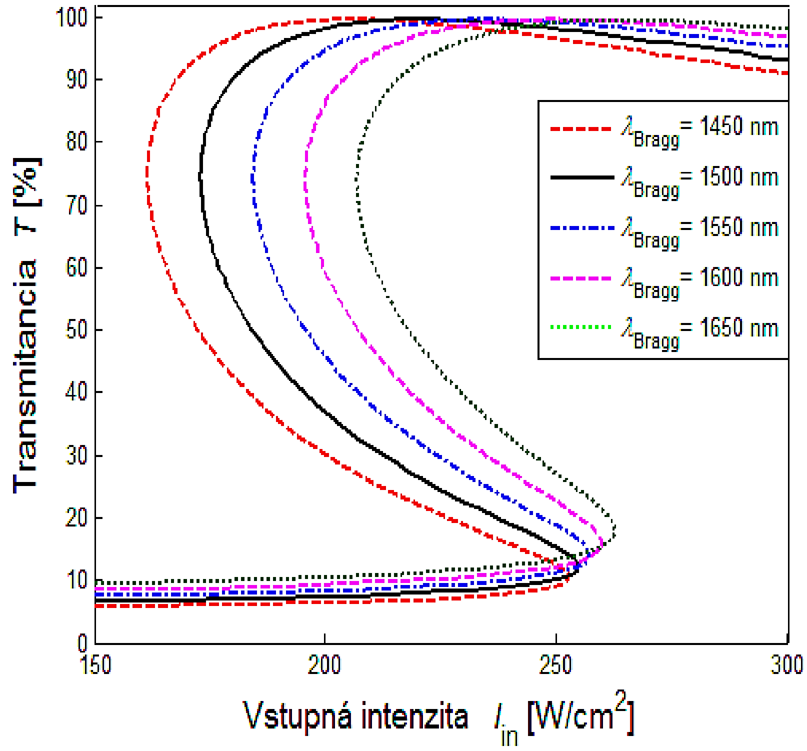


$\delta= -0.735 cm^{-1}$



λ_{Bragg}= 1550 nm , L=1 cm a

V_n=0,0001

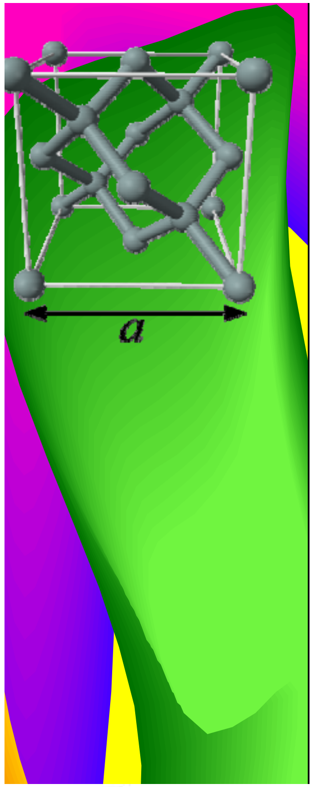


w = 72 MW/cm^2 (δ =0)

w =127 MW/cm^2 ($\delta \neq 0$)

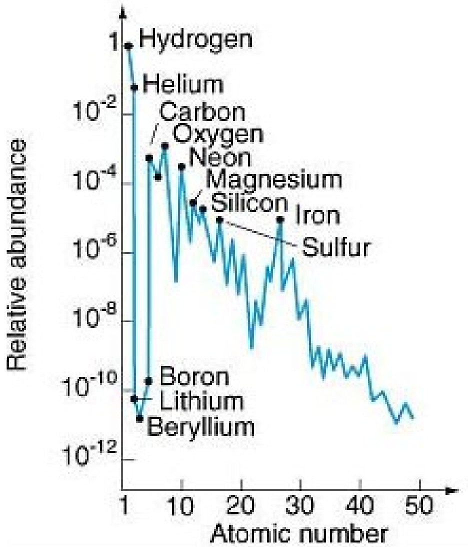
Outline

1. Introduction
2. Motivation
3. Thin films
4. Measurement techniques
5. **Photonics materials:**
    - overview
    - dielectrics
    - **group IV element based photonic materials: Si**
    - organic materials

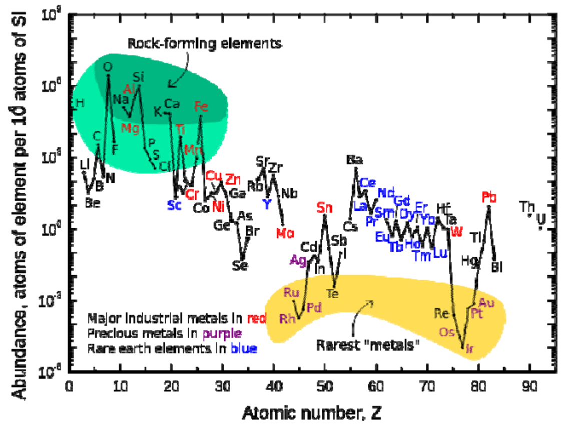


Silicon photonics

- **Silicon photonics** – engineering the optical properties of Si-based devices
- **Silicon** – overwhelmingly the dominant material for a whole range of electronic functions and circuitry
- **Comprehensive characterization** necessary for various technologies
- **Thin films of Si:H** deposited by various technologies in in various conditions



Feasible and non-destructive characterization methods – optical spectroscopies (Reflectance/Transmittance UV Vis & FTIR, ATR/HATR FTIR, Raman)

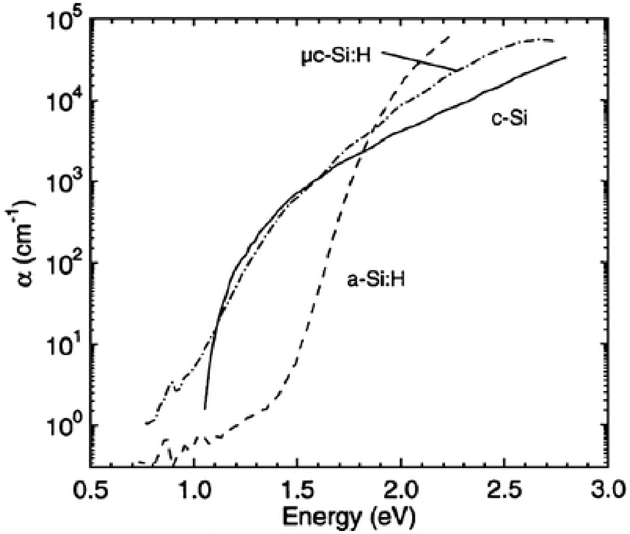


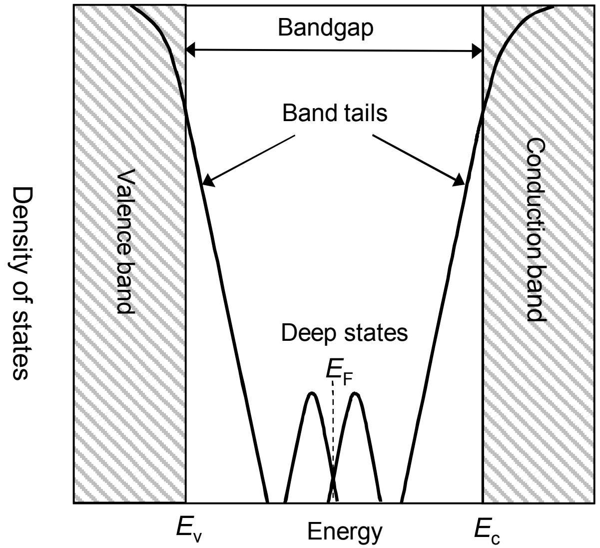
http://zebu.uoregon.edu

www.nanoHUB.org

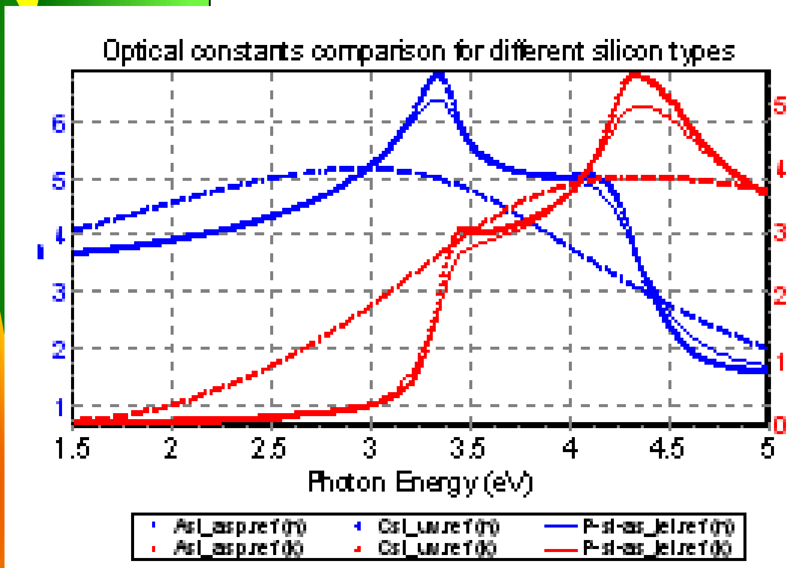
Optical properties of Si

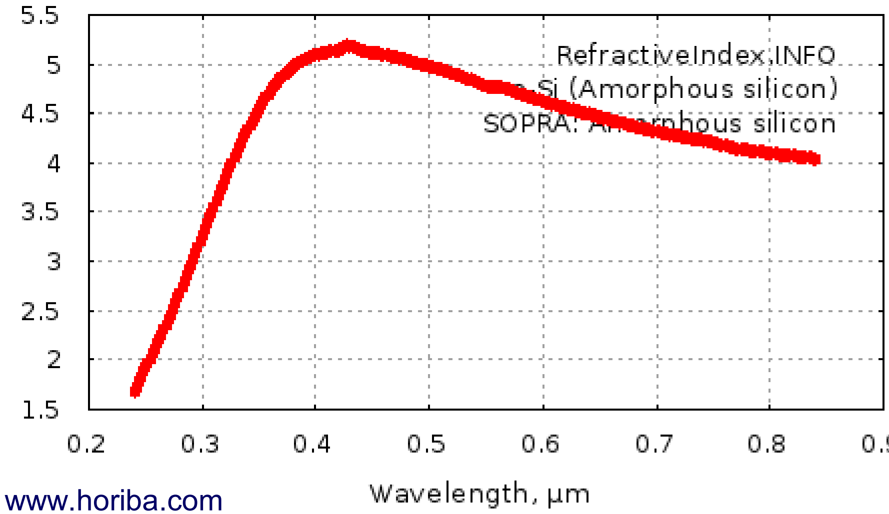
a-Si (c-Si) – direct (indirect) semiconductor





Vetterl O., et al., (2000) Sol Energy Mat Sol Cells 62: 97–108





www.horiba.com

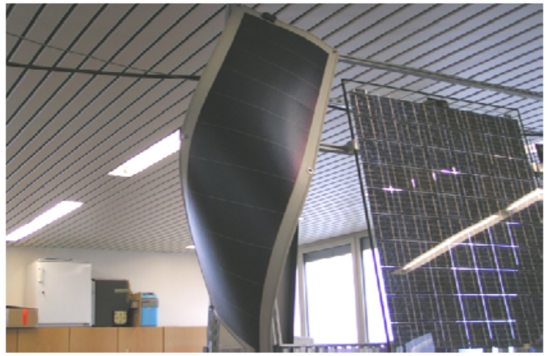
Technologically relevant Si:H

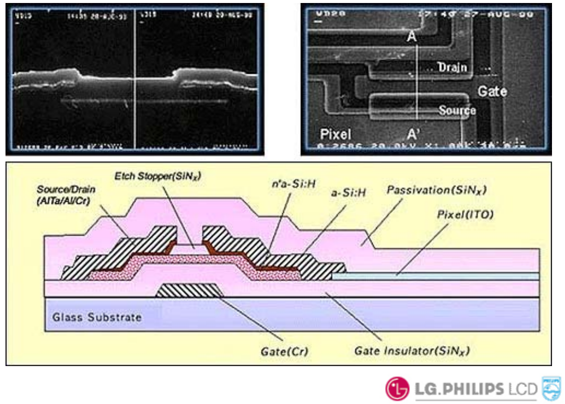
Applications: low-cost & large–area opto- and microelectronics

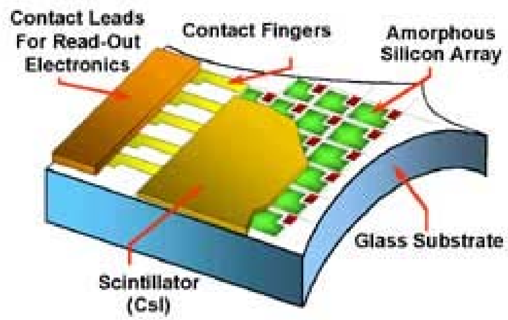
Thin-film photovoltaics –from amorphous to polycrystalline, nanocrystalline, protocrystalline Si:H … stability against prolonged solar irradiation (light soaking)

Thin-film transistors (TFT) – active display switching technologies of LCD - for laptops, displays, wall TV systems … stability against prolonged gate-voltage stress

More - optical sensitive coatings, photosensors, photodiodes for image sensors, medical imaging, waveguides for microphotonics …





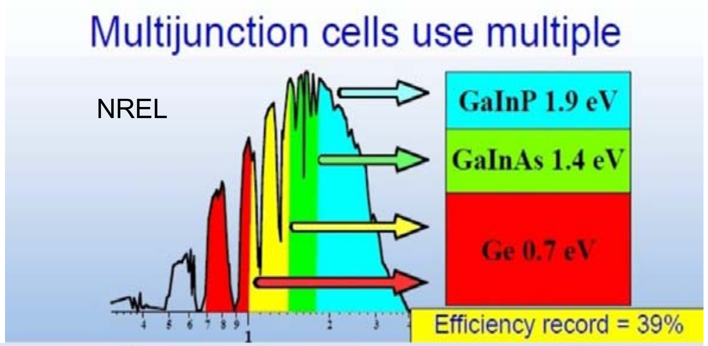


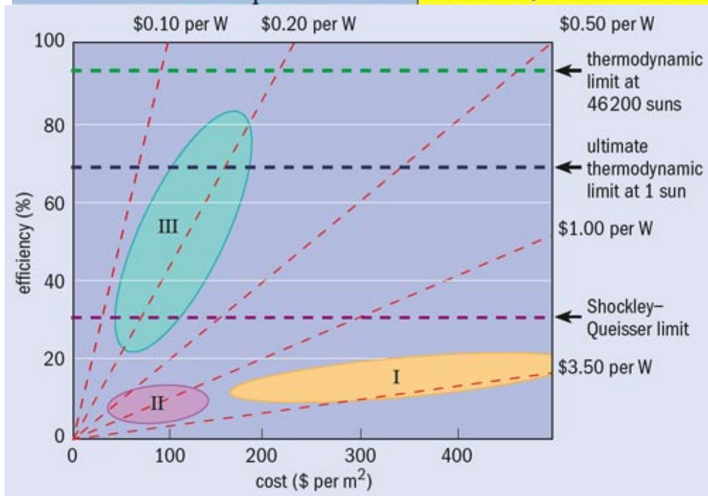
GE Revolution™ Digital Flat Panel Detector

Materials for photovoltaics

Solar cells:
1. Generation: c-Si
2. Generation: thin-film solar cells: a-Si, µc:Si, CdTe, CI(G)S
3. Generation: inovative technologies and concepts – nano-, superstructures, tandem solar cells, organic photovoltaics etc.

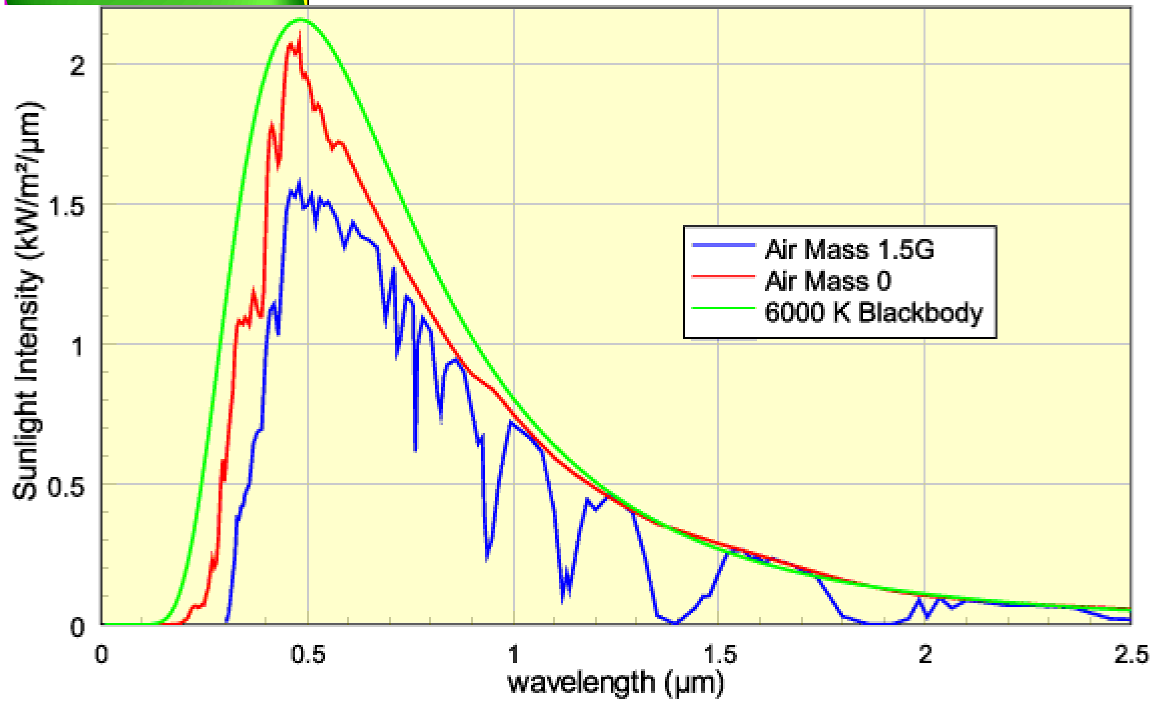
Hot news:
Ferroelectric oxides - persovskite ($CaTiO_3$)
e.g. KNO ($KNbO_3$), KBNNO
($[KNbO_3]_{1-x}[BaNi_{1/2}Nb_{1/2}O_{3-\delta}]_x$)
(J. Spanier et al. Drexel Univ., Univ. of Pennsylvania)
(first reported 2009, efficiency 3,5 %)
stabile, non-toxic, cheap
Better usage of the solar spectrum
Nature, published online 10 Nov 2013



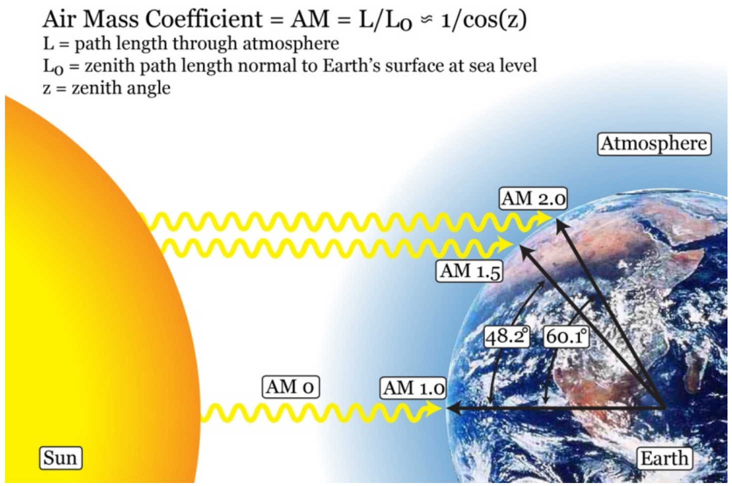


Martin Green; Nature online, Nov 2013

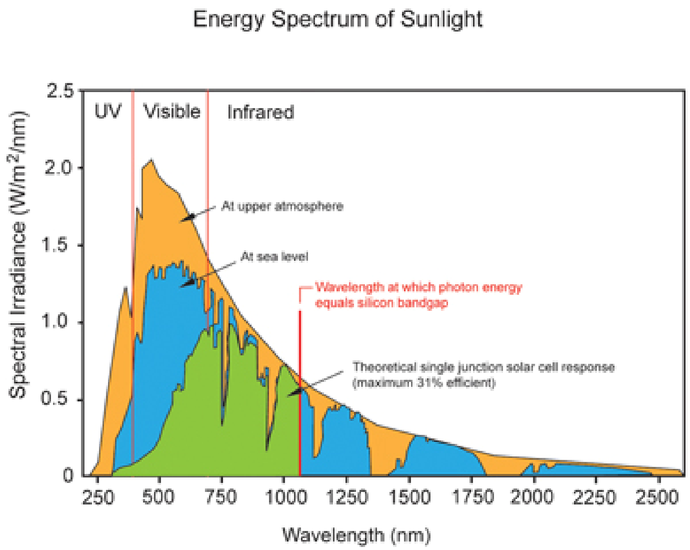
AM 1.5 solar spectrum



http://pvcdrom.pveducation.org

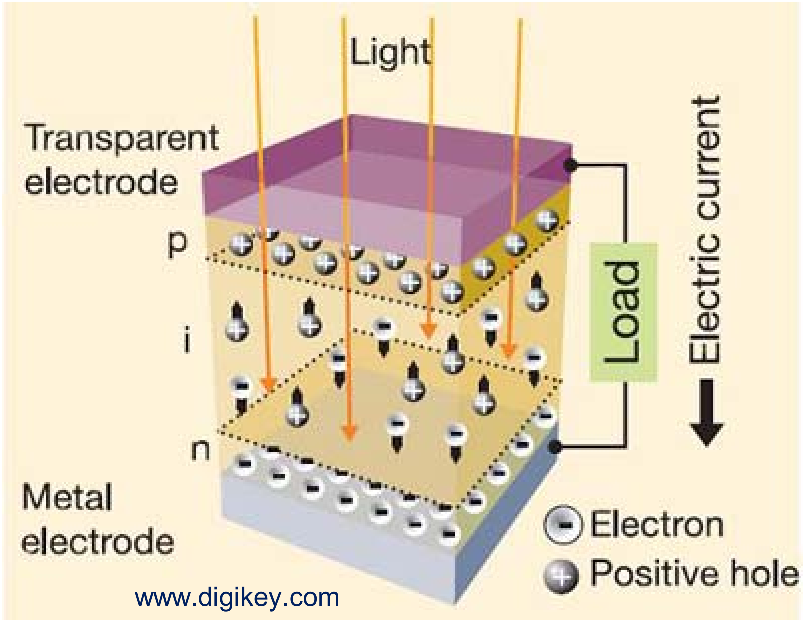


www3.nd.edu



www.viridiansolar.co.uk

Photovoltaics



PV conversion = photoelectric effect based on the separation of hole and electron pairs when exposed to light

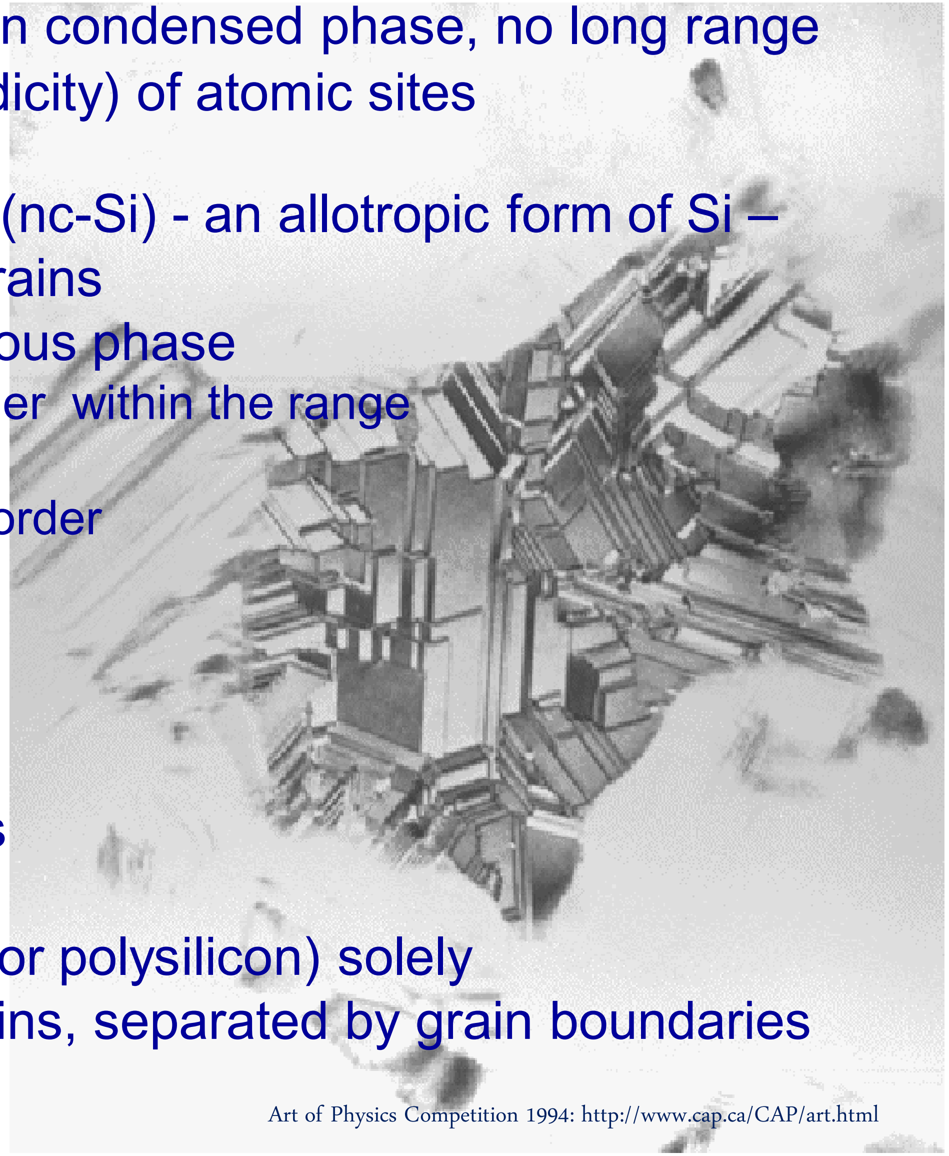
Microstructure: a-Si, nc-Si …

Amorphous Si (a-Si) is in condensed phase, no long range translational order (periodicity) of atomic sites

Nanocrystalline silicon (nc-Si) - an allotropic form of Si – similar to a-Si. nm-size grains of c-Si within the amorphous phase
Short range order - the order within the range of 0-1 nm (local order)
Medium range order - the order within the range of 1-10 nm

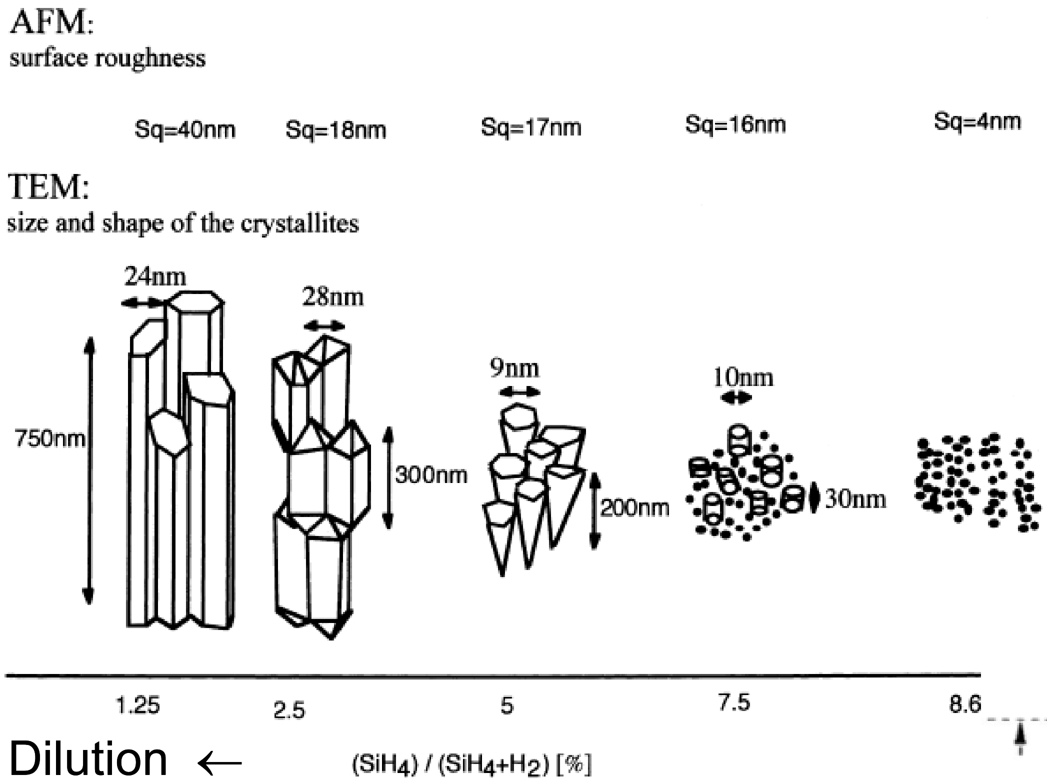
Microcrystalline silicon (μc-Si) is similar containing *μm* size grains

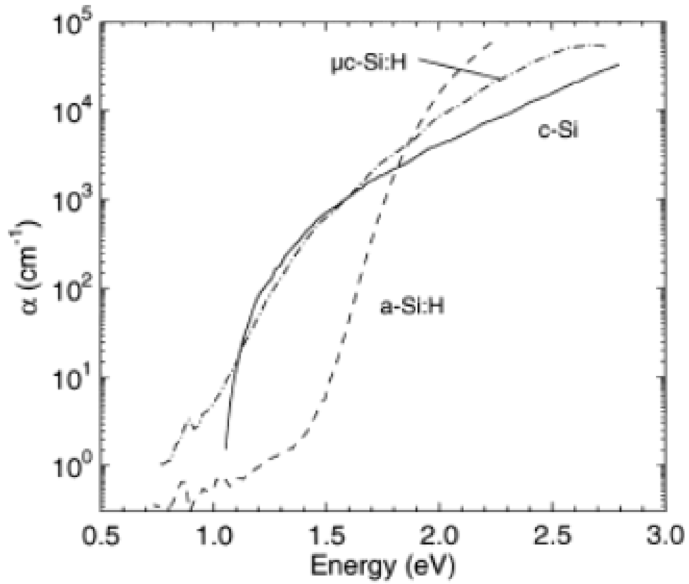
Polycrystalline silicon (or polysilicon) solely polycrystalline silicon grains, separated by grain boundaries

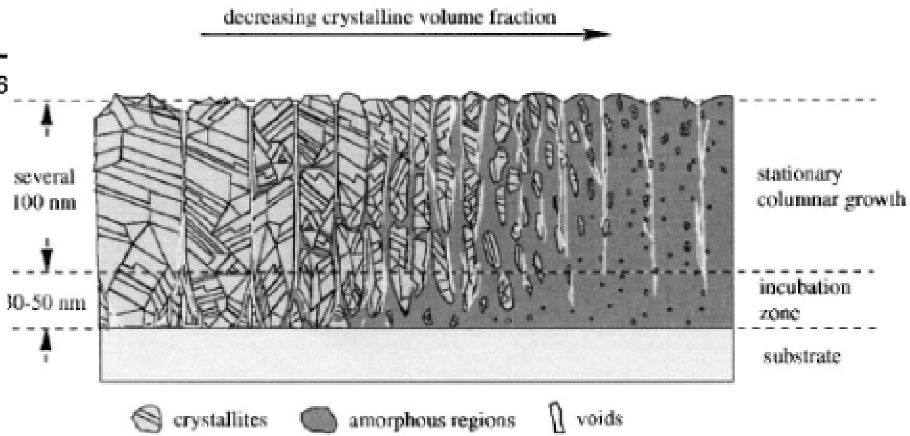


Art of Physics Competition 1994: http://www.cap.ca/CAP/art.html

PECVD structure evolution





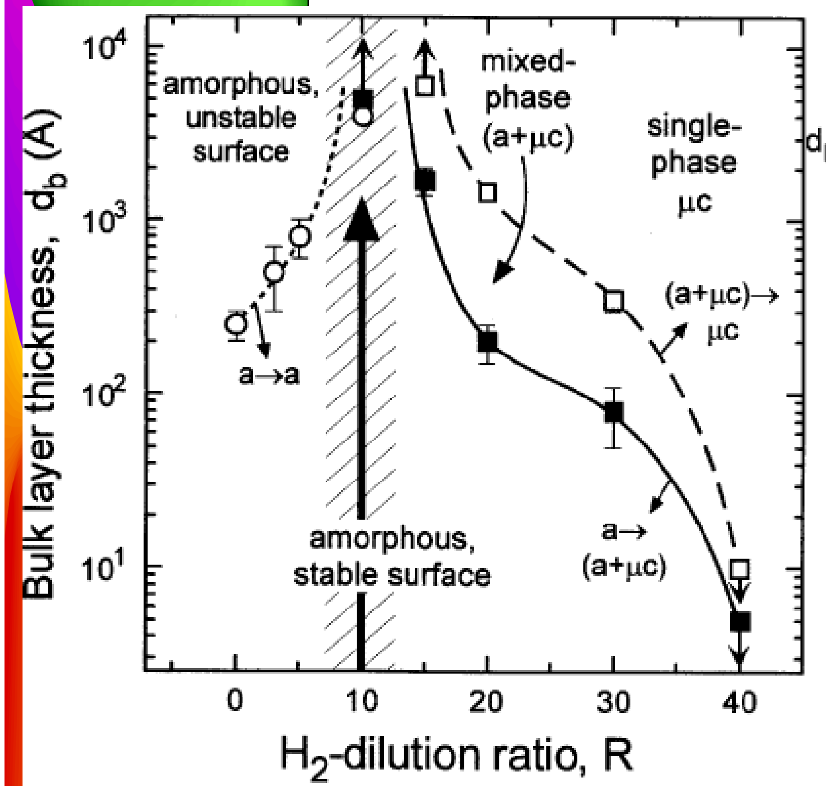


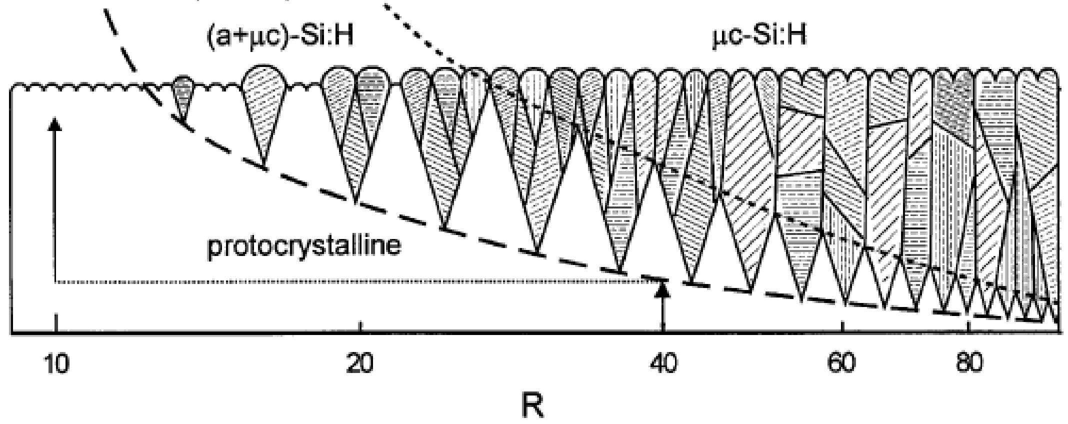
E. Vallat-Sauvain, U. Kroll, J. Meier, N. Wyrsch, A. Shah, J. Non-Crystall. Sol. 266 – 269 (2000), 125 - 130

O. Vetterl et al., Solar Energy Mat.&Solar Cells, 62 (2000), 97 - 108

Phase transition

R.W. Collins et al. / Solar Energy Materials & Solar Cells 78 (2003) 143–180





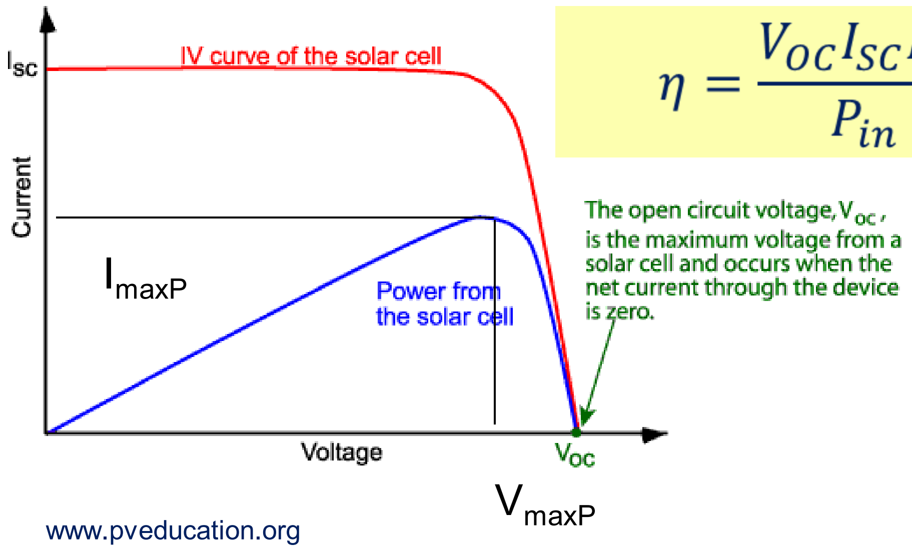
Most important features: volume fractions, spatial distribution within the films

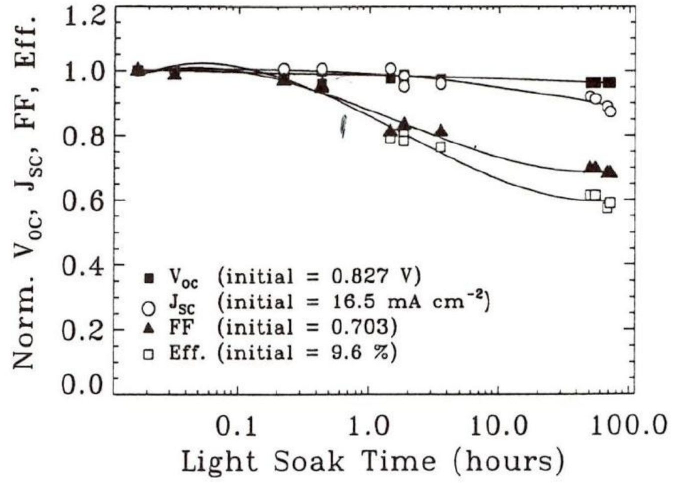
Depends on: deposition conditions – dilution, thickness, substrate …

Results in: individual structure, microstructure and subsequently optical& electrical properties

Solar cell parameters

$$\eta = \frac{V_{OC} I_{SC} FF}{P_{in}} \qquad FF = \frac{V_{OC} I_{SC}}{I_{maxP} V_{maxP}}$$





Staebler-Wronski effect = the so-called light-soaking, degradation of cell efficiency under prolonged solar irradiation due to the thermally not stable defects

(Staebler, Wronski, Appl. Phys. Lett. 31, 1972, 292),

Lowering degradation – material improvement by

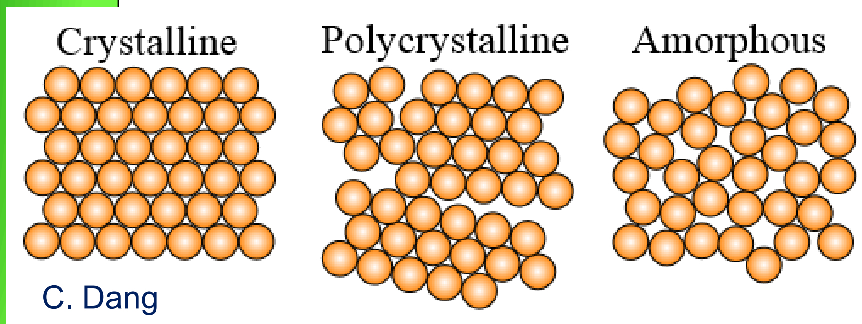
- defect passivation (passivation of dangling bonds by hydrogen) – thermal annealing
- ordering from a-Si:H to μc-Si:H

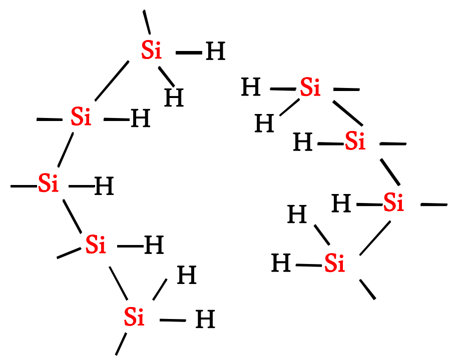
http://modtland.public.iastate.edu/seniord.html

Role of hydrogen in Si:H

- alloying
- defect compensating - passivating dangling bonds
- suppressing the metastability (Staebler-Wronski effect)
- relaxing the strained a-Si network
- ordering (improving medium-range order) – assisting crystallisation

From amorphous to polycrystalline Si:H: inhomogeneous deposition from PECVD under strong hydrogen dilution





Inspiration

"The scientist is not a person who gives the right answers, he's one who asks the right questions." Claude Levi-Strauss

Cartoon by Sidney Harris

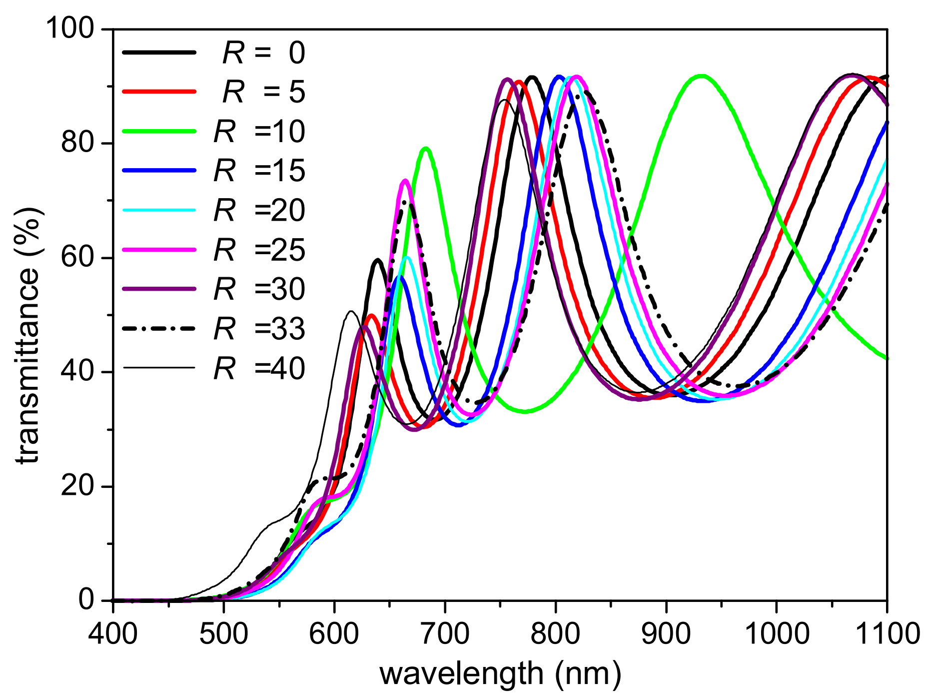
Study of Si thin films for solar cells

Thin films of intrinsic Si:H:
rf PECVD deposition
Various series: thickness, substrate temperature, dilution, substrate
Dilution of SiH_4 plasma by hydrogen = $H_2 / (H_2 + SiH_4)$

UV Vis – Specord 210, 380 – 1100 nm
FTIR – Nicolet 380, 400 – 4000 cm^{-1} equipped by ATR
Raman – Jobin Yvon HR800 (He-Ne laser)

Müllerová, J., Vavruňková V., Šutta, P. Central European Journal of Physics, 7(2), 2009
Müllerová, J., *et al.* Applied Surface Science 254 (2008) 3690–3695

Optical spectra



$$\varepsilon_1(\omega) = n^2(\omega) - k^2(\omega)$$

$$\varepsilon_2(\omega) = 2n(\omega)k(\omega)$$

Tauc - Lorentz dispersion:

$E > E_g$

$$\varepsilon_2(E) = \frac{1}{E}\frac{A_L E_L C_L (E - E_g)^2}{(E^2 - E_L^2)^2 + C_L{}^2 E^2}$$

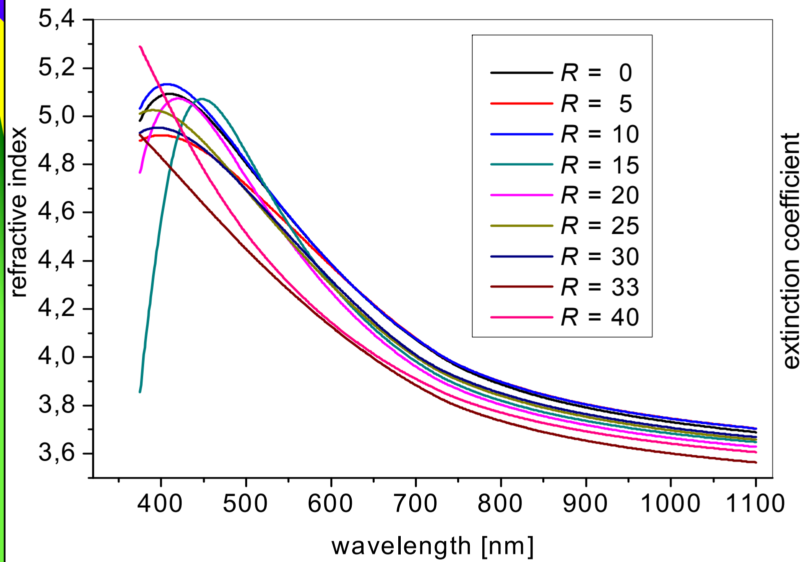
$E < E_g$

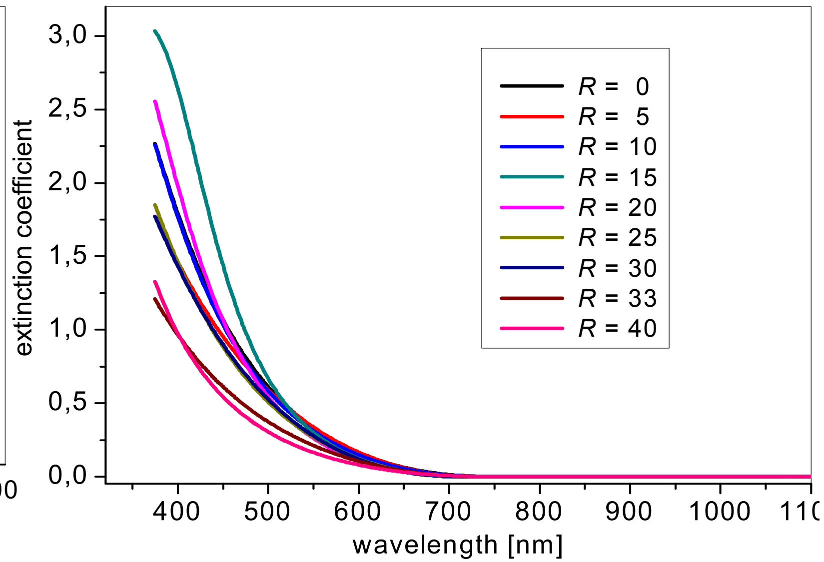
$$\varepsilon_2(E) = 0$$

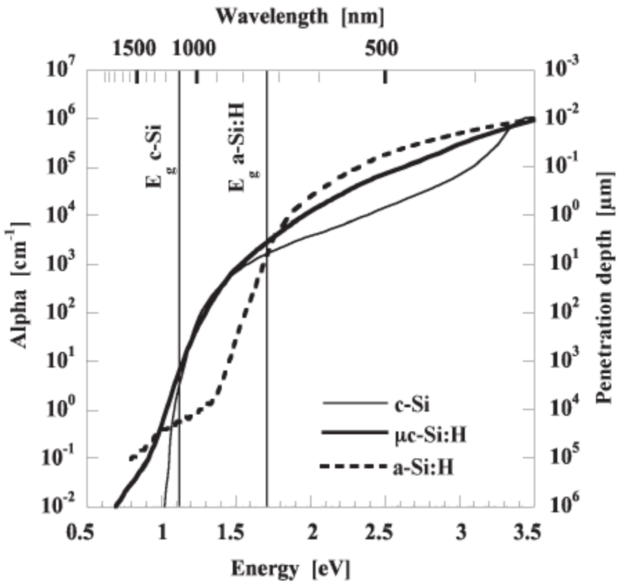
E_L – the Lorentz's resonance energy, C_L – the broadening parameter, A_L – a constant. The real part of the permittivity – determined by the Kramers – Kronig integration

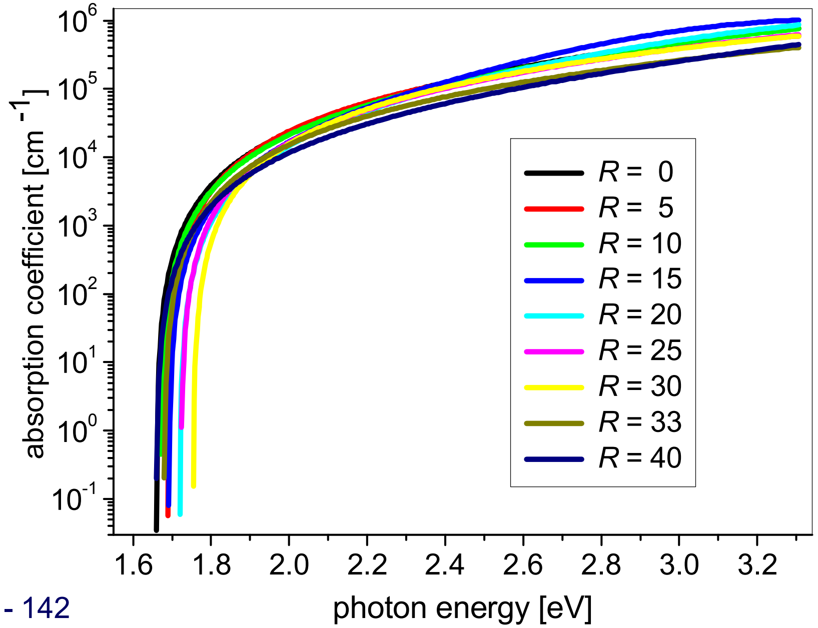
Jellison, G.E. Jr., Modine, F.A., Appl. Phys. Lett. vol. 69, 1996, 371 – 373

Optical properties









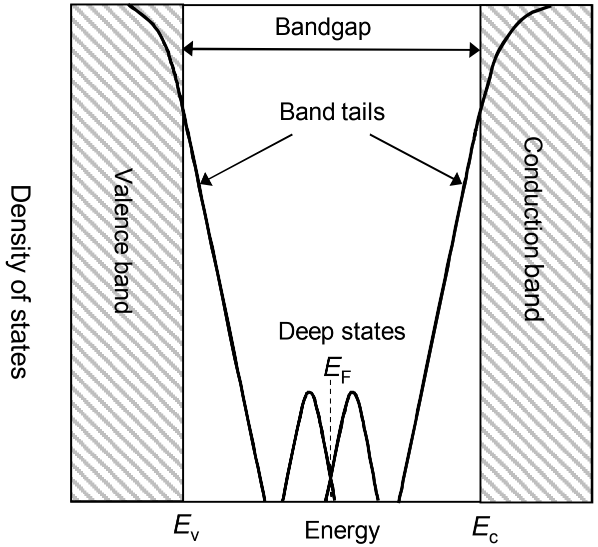
A.V.Shah *et al.*, Prog. Photovolt: Res. Appl.2004, 12, 113 - 142

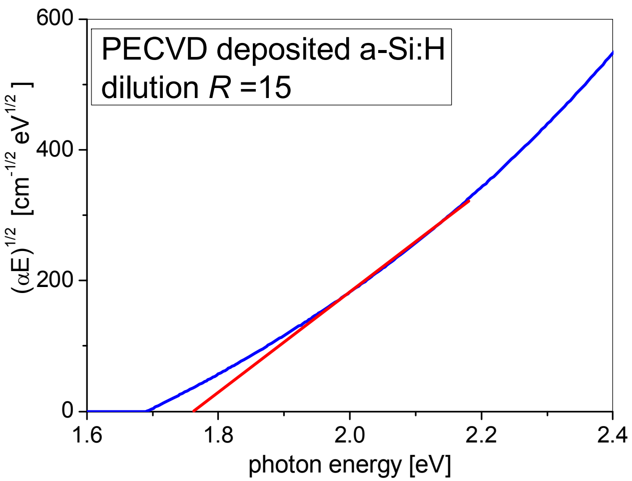
Tauc optical band gap & *B*-factor

Jan Tauc
(1922-2010)

E_g ... the Tauc band gap energy absorption is dominated by band-to-band transitions (between extended states of valence and conduction bands)

$$(\alpha E)^{1/2} = B(E - E_g)$$





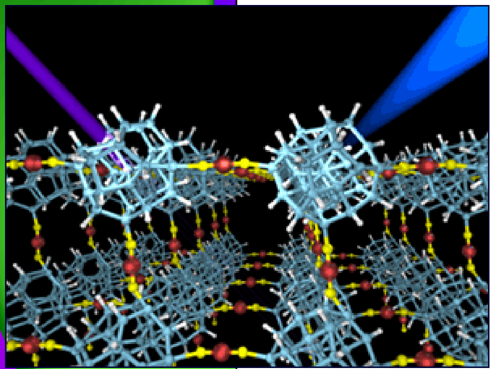
***B* ... the scaling factor**

the slope of the straight-line part of the plot

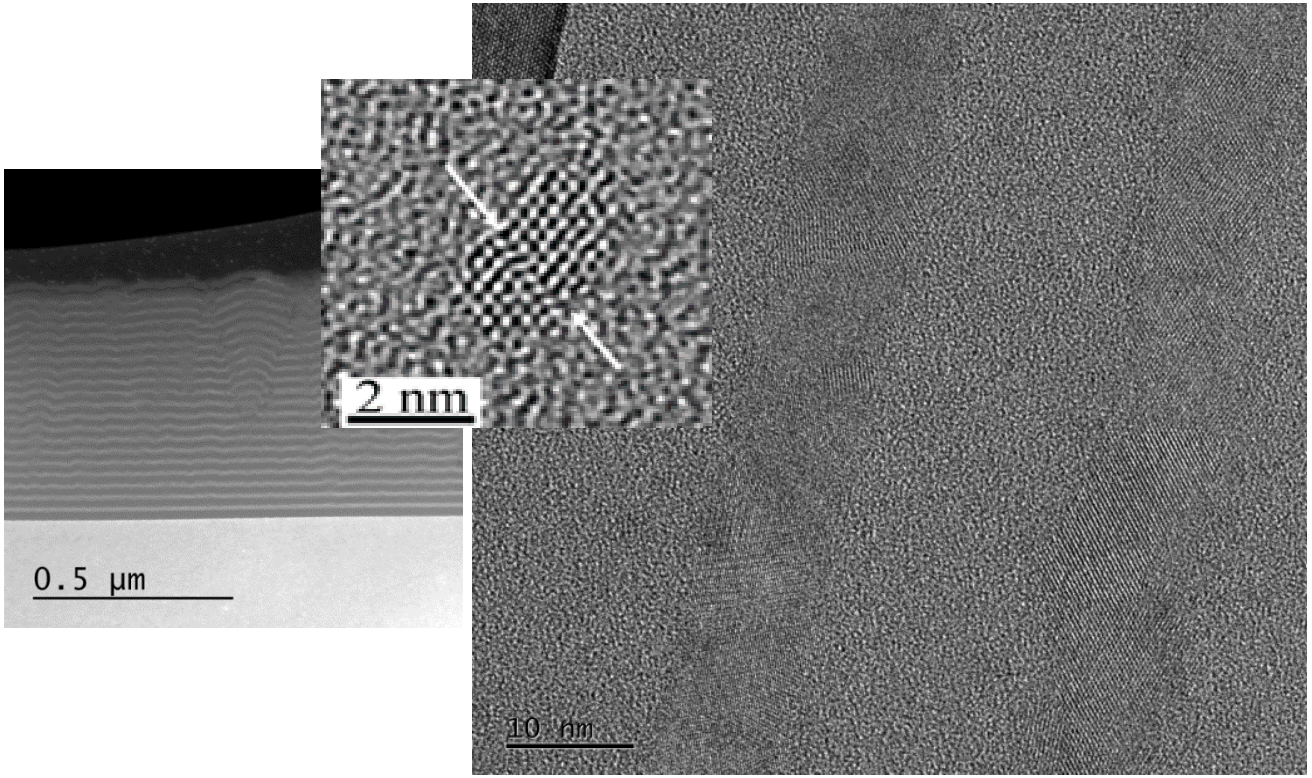
- the convolution of the VB and CB states
- correlated to the structural and compositional disorder and the band-edge modifications
- depends on the product of the optical transition oscillator strength, the deformation potential and mean bond angle distribution

Bibhu B. Swain *et al.*: Thin Solid Films 430 (2003) 186 – 188; J.P. Conde *et al.*: J. Appl. Phys. 85, 6 (1999) 3327 – 3338; A.R. Zanatta, I. Chambouleyron, Phys. Rev. B 53, 7 (1996) 3833 - 3836

Confined systems



dilution	E_g [eV]	QD a [nm]
0	1.71	3.87
5	1.72	3.71
10	1.73	3.59
15	1.76	3.32
20	1.78	3.16
25	1.77	3.24
30	1.78	3.16
33	1.72	3.71
40	1.71	3.82



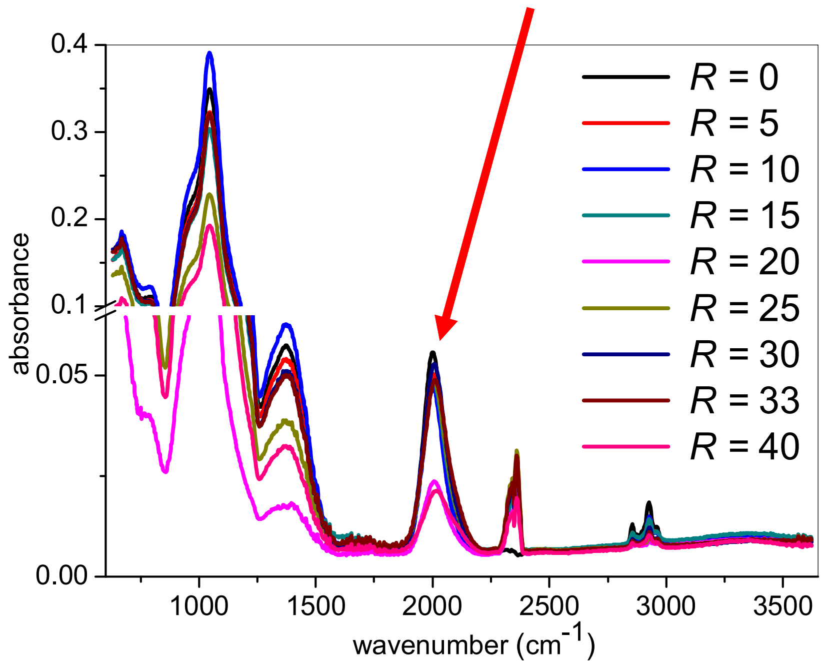
Shift of E_g: grain size effect

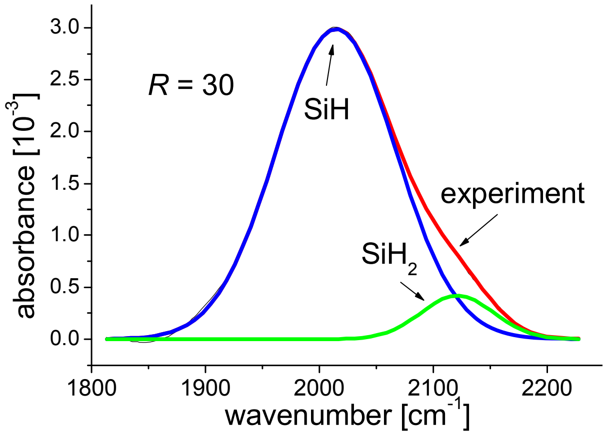
Kayanuma's equation (eV, nm) - quantum dots

$$E_g^{opt} = 1.56 + 2.2 / a^2$$

physci.llnl.gov/.../siliconDots_stokes.html, P. Šutta, osobné oznámenie okt. 2013, Chaudhuri, P. et al: J. Non-Cryst. Solids 338 – 340 (2004), 236, Müllerová, J., Vavruňková, V., Šutta, P.: Advances in Electrical and Electronic Engineering. No. 1 – 2, vol.7, 2008, 369 – 372

FTIR absorbance





Bonding		Mode assignment	wavenumber [cm^{-1}]
SiH_x (x = 1, 2, 3)	Hydride	Rocking, wagging	630 – 670
Si-O-Si	Interstitial oxygen	Stretching (weak)	780 – 800
SiH_x (x = 1, 2, 3)	Hydride	Bending (weak)	845 – 910
Si-O-Si	Interstitial oxygen	Assymetric stretching	940 – 1030
SiH	Hydride	Stretching	2000
SiH_2	Hydride	Stretching	2100
Si-OH	silanol	Stretching	3000 - 3700

Role of hydrogen

H content: analysis of stretching vibrations of Si–H bonds at ~ 2000 cm^{-1}

$$c_{\mathrm{H}} = \frac{A_x}{N_{\mathrm{int}}} \int \frac{\alpha(\bar{\nu})}{\bar{\nu}} d\bar{\nu}$$

$$A_x = 9 \times 10^{19}\,\mathrm{cm}^{-2}$$

$$N_{\mathrm{int}} = 5 \times 10^{22}\,\mathrm{cm}^{-3}$$

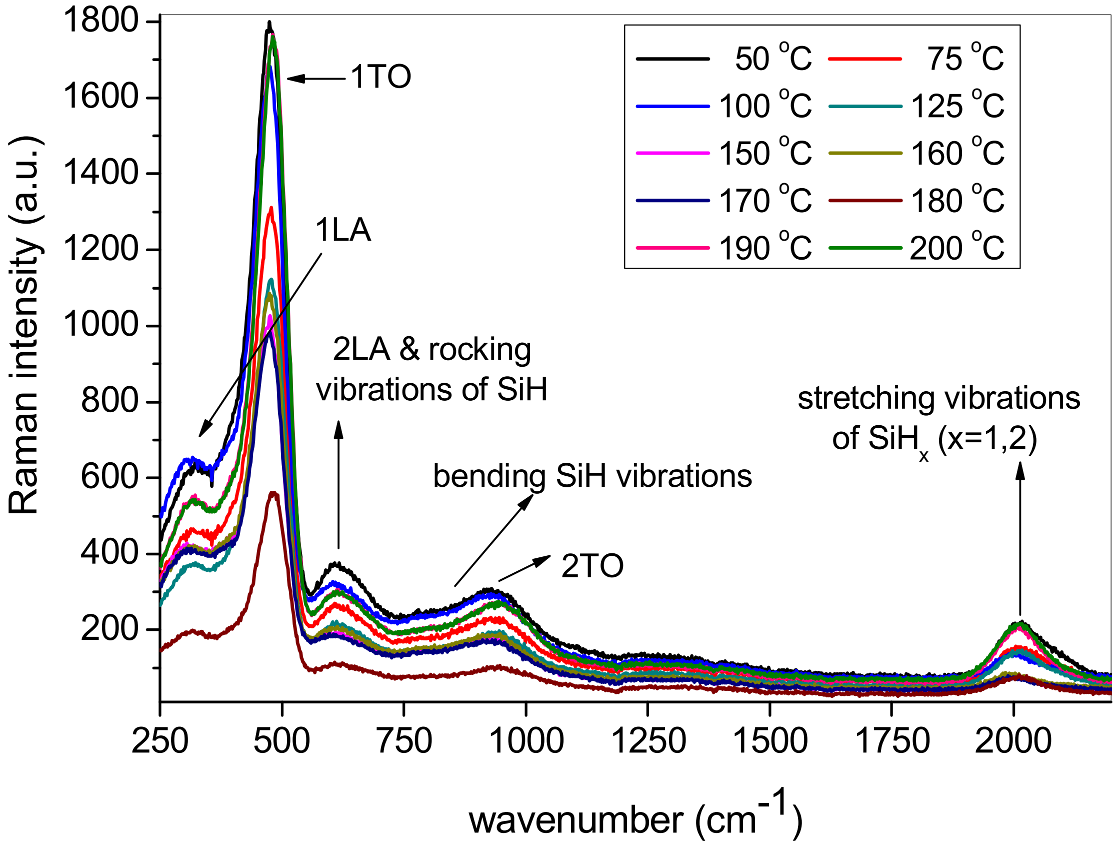
Microstructure factor:
the figure of merit of the homogeneity of the film

$$\mu = \frac{\int A_{\mathrm{SiH}_2}(\bar{\nu})d\bar{\nu}}{\int A_{\mathrm{SiH}_2}(\bar{\nu})d\bar{\nu} + \int A_{\mathrm{SiH}}(\bar{\nu})d\bar{\nu}}$$

dilution	μ	c_{H} [%]
0	16.28	16.49
5	11.05	14.20
10	9.14	13.24
15	13.23	14.61
20	14.42	6.82
25	11.36	15.39
30	10.78	16.76
33	12.66	16.78
40	13.96	6.72

⇒ **porousity !**

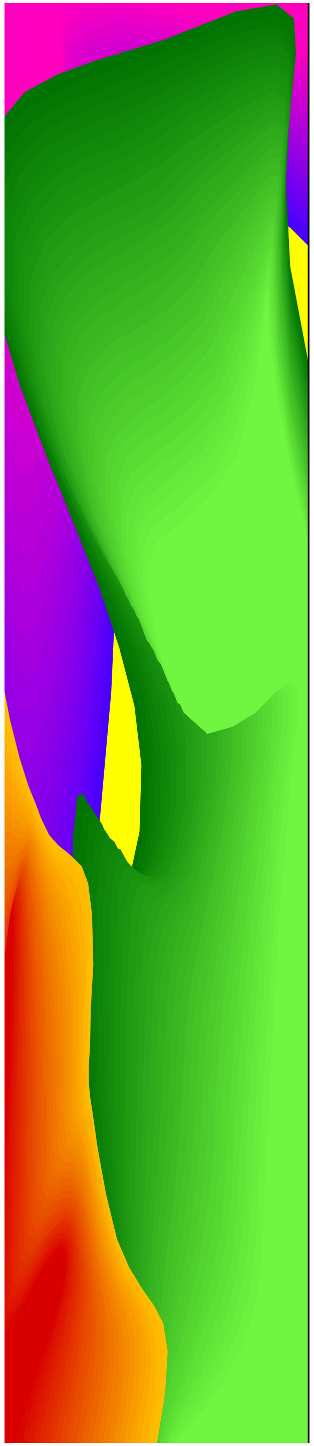
A closer look: Raman scattering

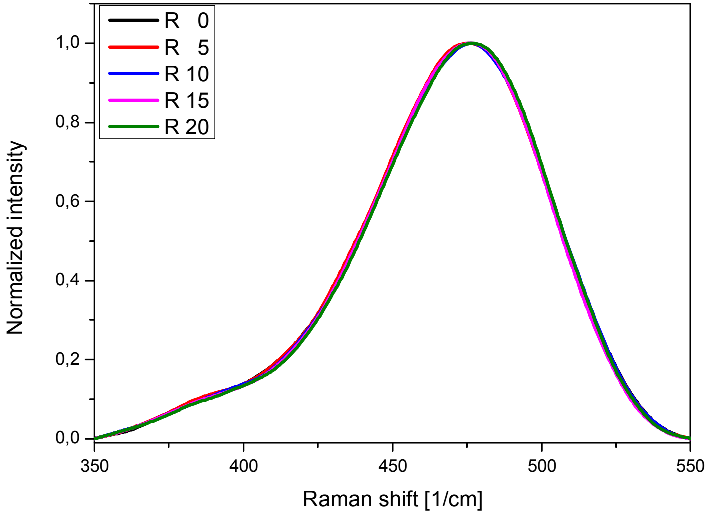


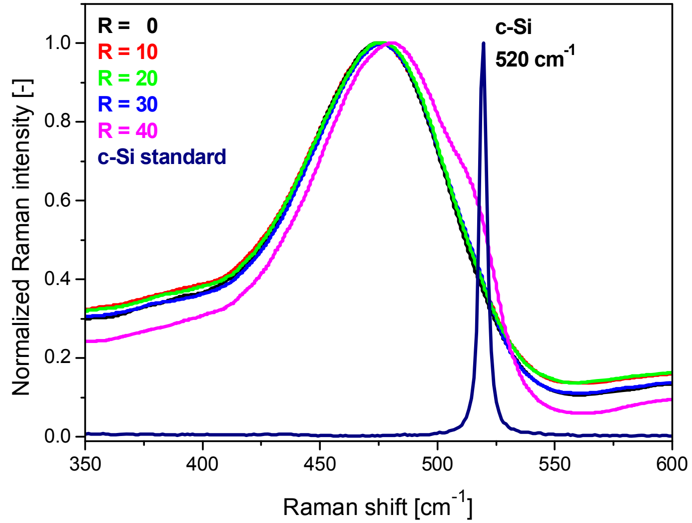
Crystalline to amorphous volume fraction: degree of crystallinity

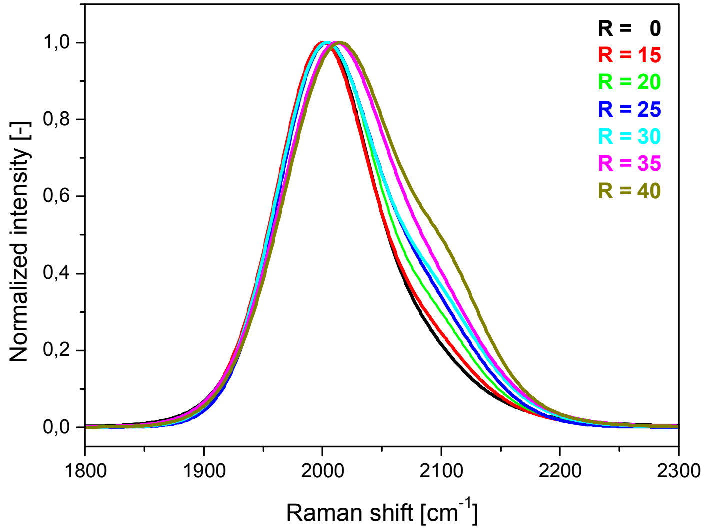
$$x_c = p_c/(p_a + p_c) = \frac{\int I_{520}(\bar{v})d\bar{v}}{\int I_{480}(\bar{v})d\bar{v} + \int I_{520}(\bar{v})d\bar{v}}$$

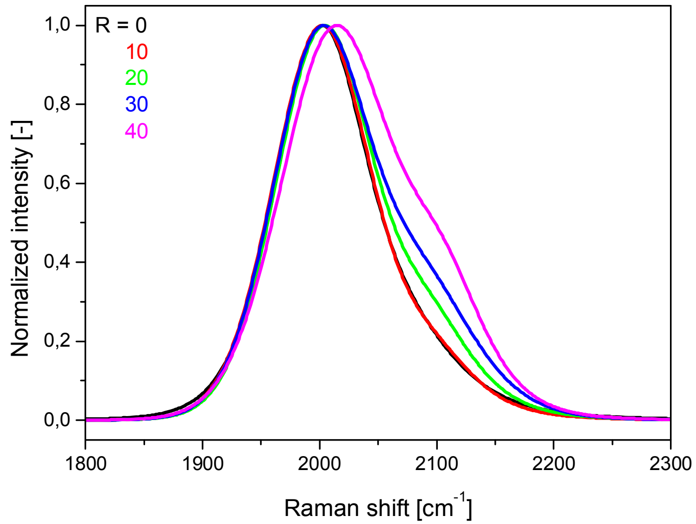
Multiphase material





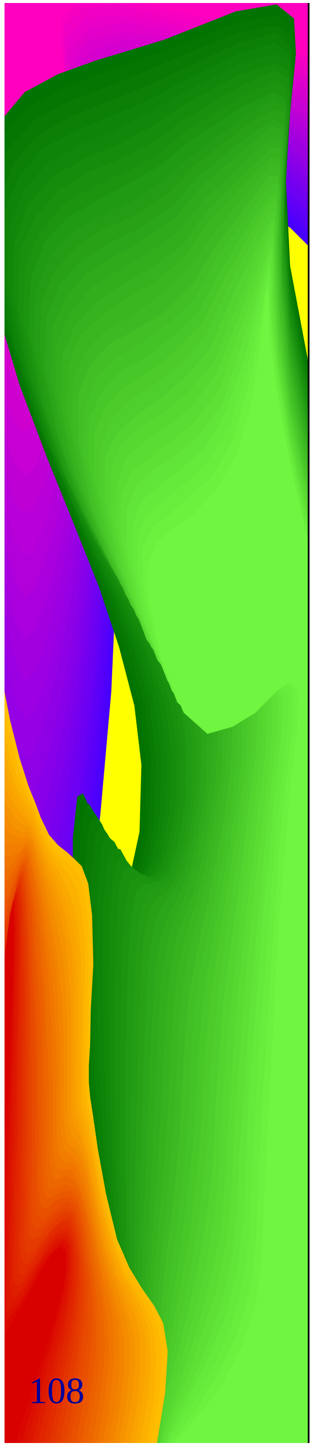






By courtesy of Pavel Šutta, Univ. of West Bohemia, Plzeň, the Czech Republic

Deconvolution model



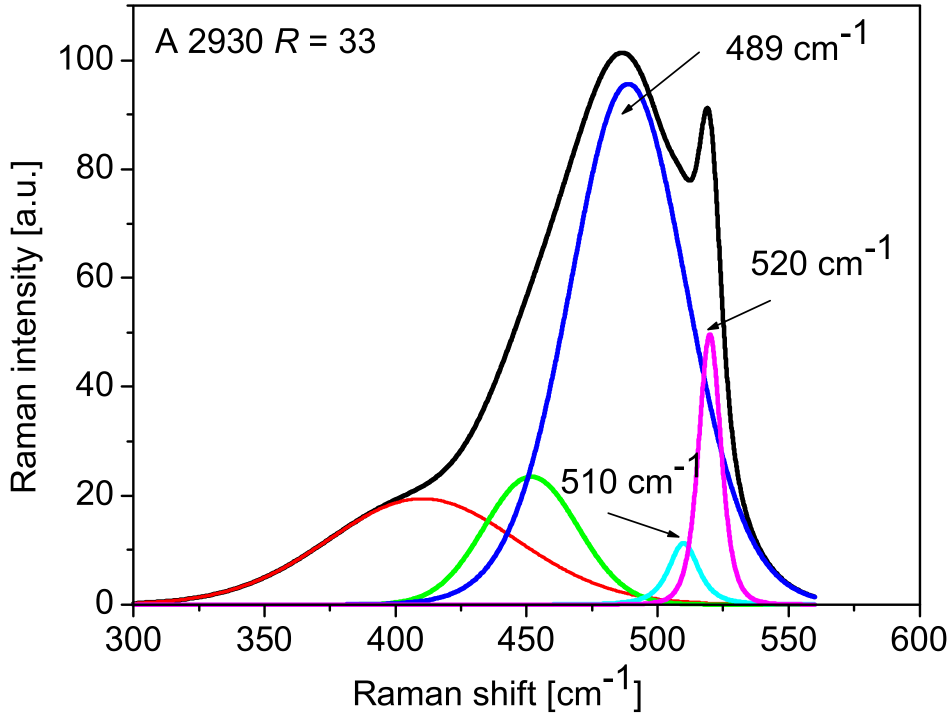
Conventional approach:
- a-Si
- mean single crystalline grains

More realistic model:
- a-Si ~ 480 cm^{-1}
- large crystalline grains ~ 520 cm^{-1}
- small crystalline grains ~ 505 cm^{-1}

Grain size from Raman shift:

$$L_R = \sqrt{\frac{88.43}{\Delta \bar{\nu}}}$$

$$\Delta \bar{\nu} = \left| \bar{\nu} - 520.7\,\mathrm{cm}^{-1} \right|$$



D. Gracin *et al.*, Vacuum 82 (2008), 205 – 208, A. Gajović *et al.*, Appl. Surf. Science 254 (2008), 2748 – 2754 (using HRTEM, XRD, Raman spectroscopy and GISAXS)

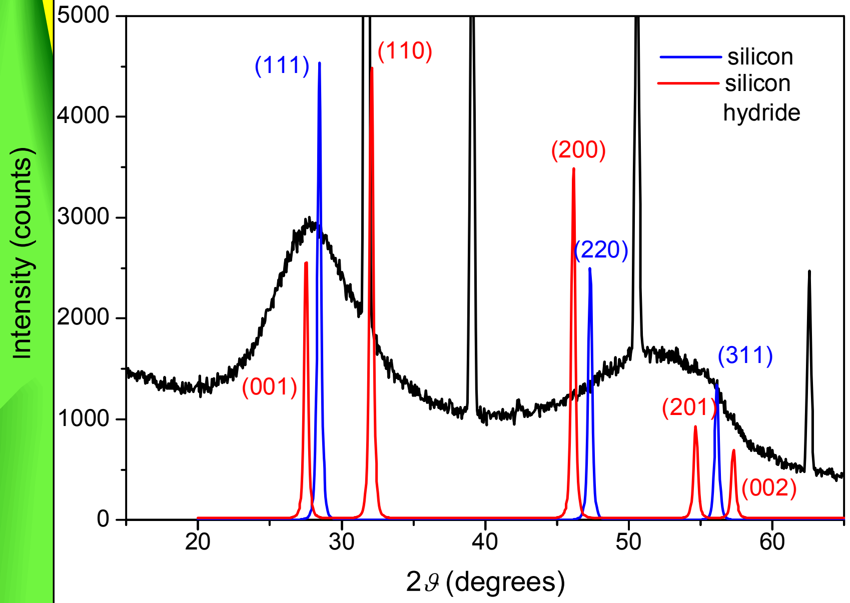
Degree of crystallinity & grain size

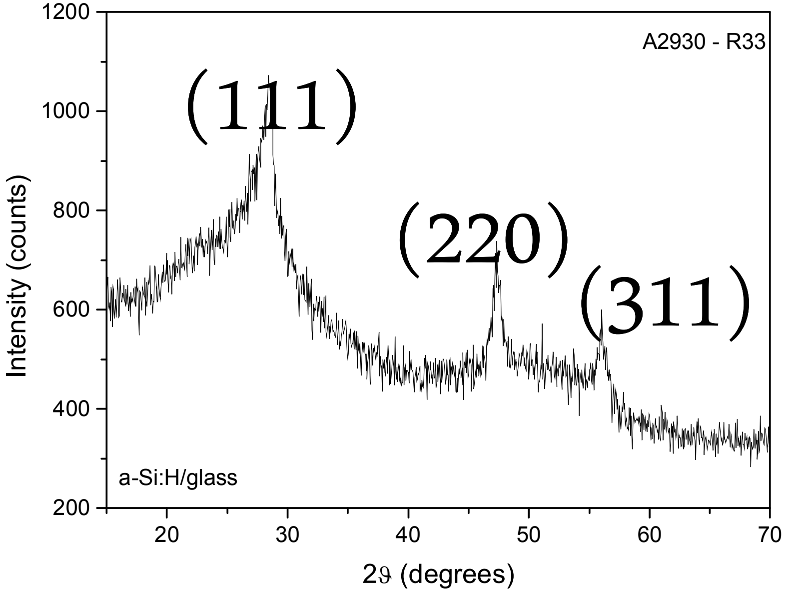
$$p_c / p_a = \frac{\int I_{520}(\overline{v})d\overline{v} + \int I_{505}(\overline{v})d\overline{v}}{\int I_{480}(\overline{v})d\overline{v}}$$

dilution	x_c [%]	p_c/p_a [%]
0	-	-
5	-	-
10	-	-
15	-	-
20	3.4	3.6
25	1.7	1.7
30	6.3	6.8
33	12.3	14.0
40	57.4	134.7

R	x_c [%]	p_c/p_a [%]	L_R (small) [nm]	L_R (large) [nm]
20	3.4	3.6	2.4	-
25	1.7	1.7	2.6	-
30	6.3	6.8	2.7	-
33	12.3	14.0	2.9	11
40	57.4	134.7	2.3	9

Verification





Under increasing dilution the transition from amorphous Si:H to the tri-phasic μc-Si:H occurs that is reported to consist of crystalline and amorphous phase and voids

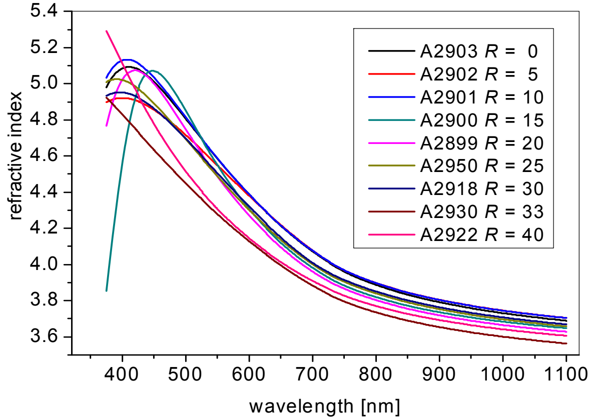
Müllerová, J. et al.: Microstructure of hydrogenated silicon thin films prepared from silane diluted with hydrogen. Appl. Surf. Sci. 254, 2008, 3690 - 3695

Müllerová, J., Vavruňková, V., Šutta, P.: Optical absorption in PECVD deposited thin hydrogenated silicon in light of ordering effects. Centr. Eur. J. Phys., 7, 2009, Issue 2, 315-320

Müllerová, J. et al.: Influence of deposition temperature on amorphous structure of PECVD deposited a-Si:H thin films. Centr. Eur. J. Phys., 9, No.5, 2011, 1301 – 1308

BEMA & volume fractions

$$p_a \frac{n_{a-Si:H}^2 - n_\infty^2}{n_{a-Si:H}^2 + 2n_\infty^2} + p_c \frac{n_c^2 - n_\infty^2}{n_c^2 + 2n_\infty^2} + + p_v \frac{1 - n_\infty^2}{1 + 2n_\infty^2} = 0$$

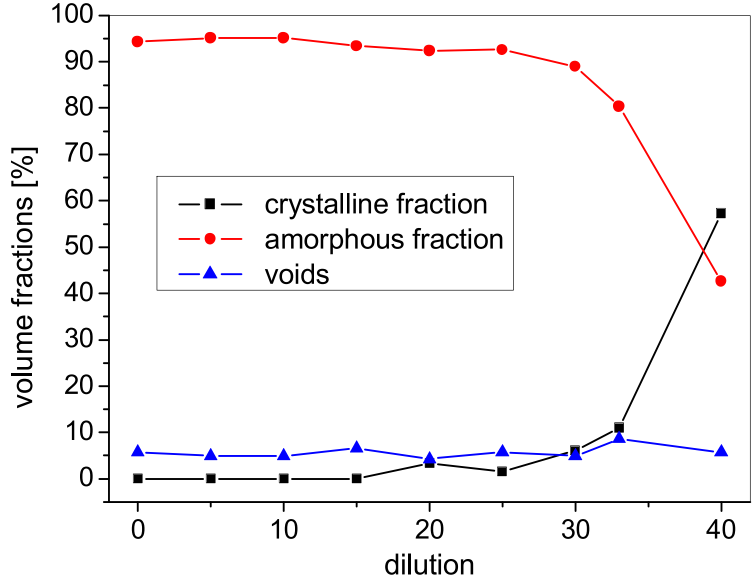


$p_c + p_a + p_v = 1$

p_c/p_a from Raman data

$$n_{eff} = n_\infty$$

Refractive index
in the long-wavelength limit
(non-absorbing region)

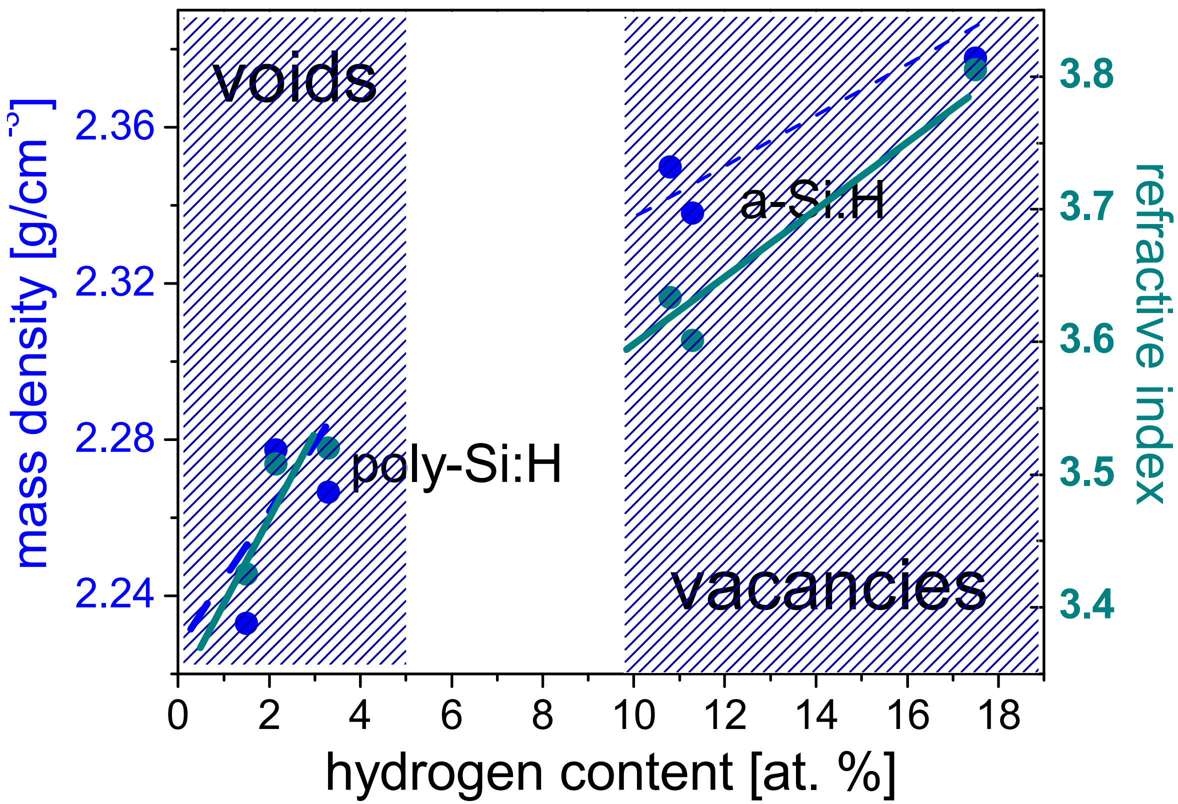


$n_{a\text{-}Si:H}$ = 3.805 *, n_c = 3.420 **
n_v = 1.0 (air)

* Müllerová, J., Šutta, P., van Elzakker, G., Zeman, M., Mikula, M.:. Appl. Surf. Science 254, 2008, 3690–3695
** Z. Remeš, M. Vaněček, P. Torres, U. Kroll, AH. Mahan, R.S. Crandall: J. Non-Cryst. Solids 227-230 (1998) 876

Inter- & intragrain microstructure

1. low hydrogen content, poly-Si:H, void-dominated network
2. higher hydrogen content, a-Si:H, vacancy-dominated network



Outline

1. Introduction
2. Motivation
3. Thin films
4. Measurement techniques
5. **Photonics materials:**
   - overview
   - dielectrics
   - group IV element based photonic materials: Si
   - **organic materials**

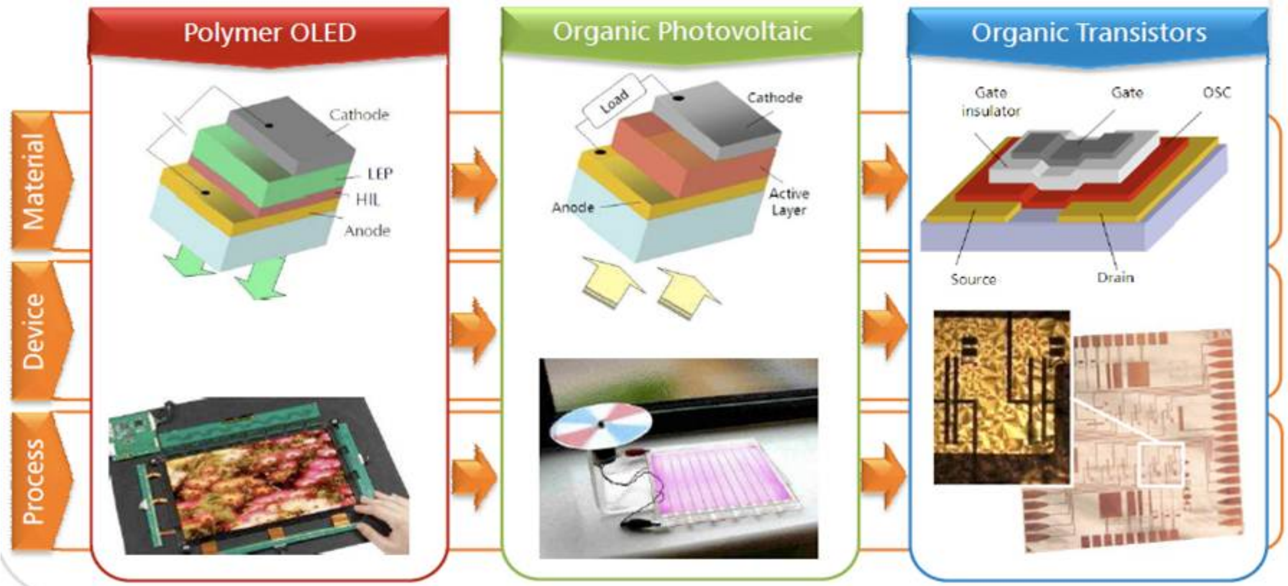
Organic photonics

Advantages:

- cheap deposition techniques (spin-coating, drop-casting, roll-to-roll processing, screen printing …)
- flexible, lightweight, portable (fashionable ☺) devices

Applications:

- organic photovoltaics
- organic light sources - lasers and OLEDs
- organics electronics - sensors, transistors (OFETs)…
- bioelectronics, medical diagnostics

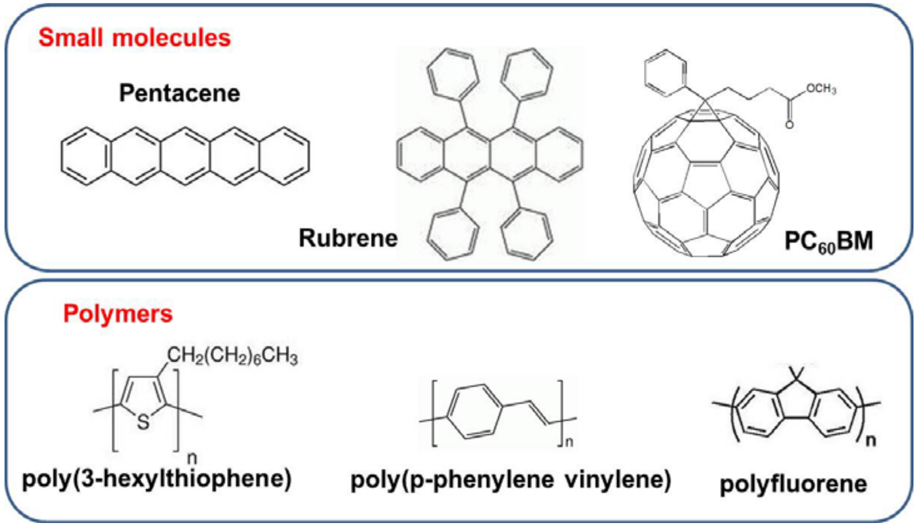


 Cambridge Display Technology, 2008

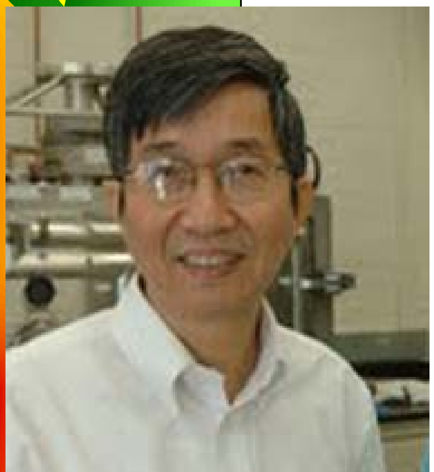
Organic photonics

= a branch of material science dealing with two types of conductive or semiconducting carbon-based molecules:

- small molecules
- polymers



http://web.donga.ac.kr/seojh/Research_OrganicMaterials.html



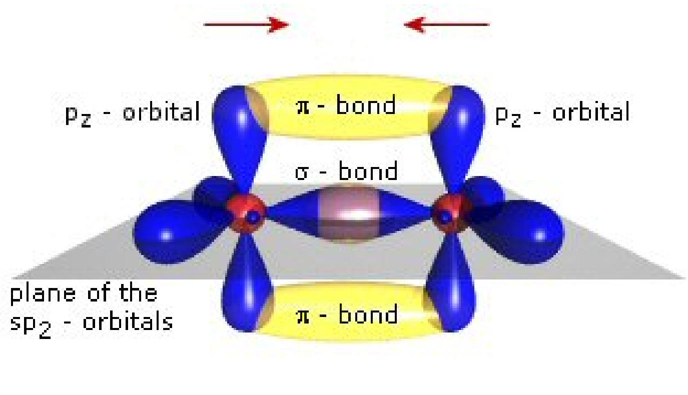
Ching W. Tang (1947) – Univ. of Rochester, American physical chemist - father of organic electronics: built the first organics light-emitting diode (OLED) and organic photovoltaic cell

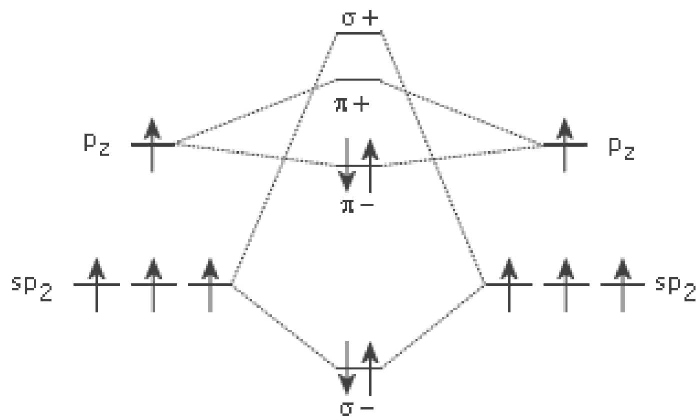
Bonds of two carbon atoms

The so-called sp_2-hybridisation in carbon atoms:

- sp_2-orbitals form a triangle within a plane
- the p_z-orbitals are in the plane perpendicular to it

σ -bond between **two carbons** is formed by an orbital overlap of two sp_2-orbitals. The energy difference between the highest occupied orbitals (HOMO) and the lowest unoccupied orbitals (LOMO) is quite large and well beyond the visible spectral range.
π –bonds of much smaller energetic difference between the HOMO and LUMO - strong absorption in or near the visible spectral range and **leads to semiconducting properties:**



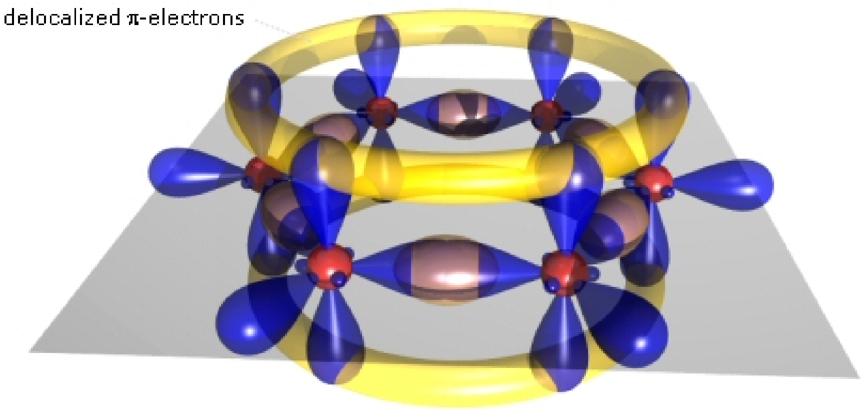


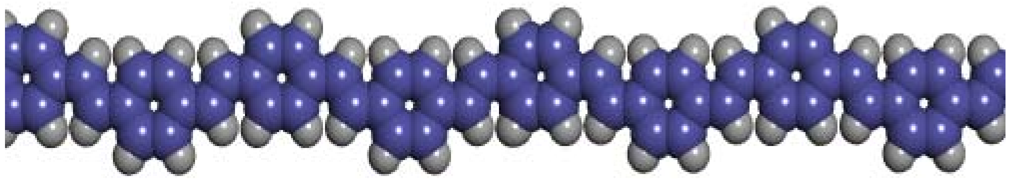
http://www.iapp.de/orgworld

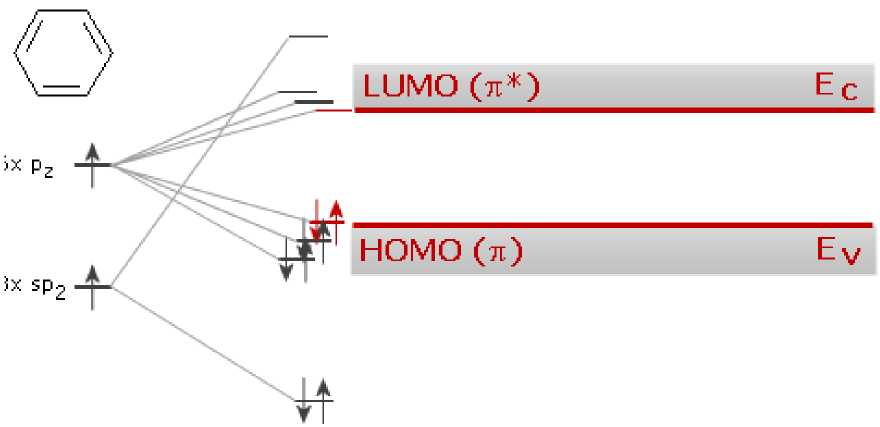
Delocalization of electrons

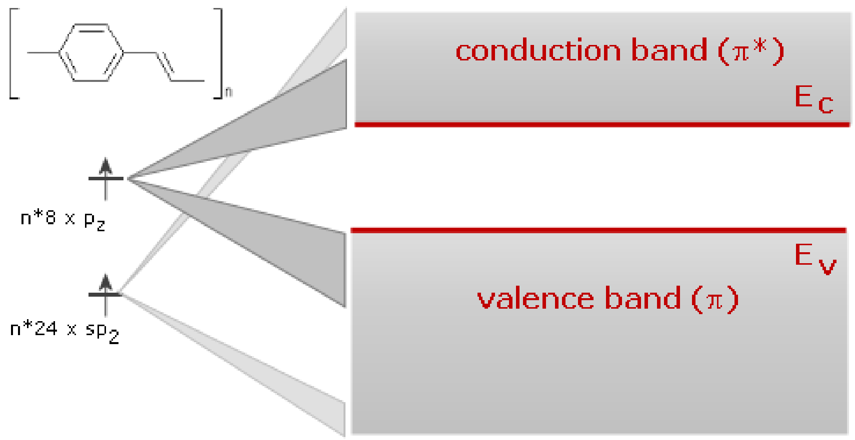
Small molecules: π-bonds delocalized of the extensions of the molecule. The gap between occupied and empty states in these π -systems ~ smaller with increasing delocalization

Polymers: π-bonds delocalized along the chain, 1D electronic semiconducting system with C- and V-band, bandwidth ~eV

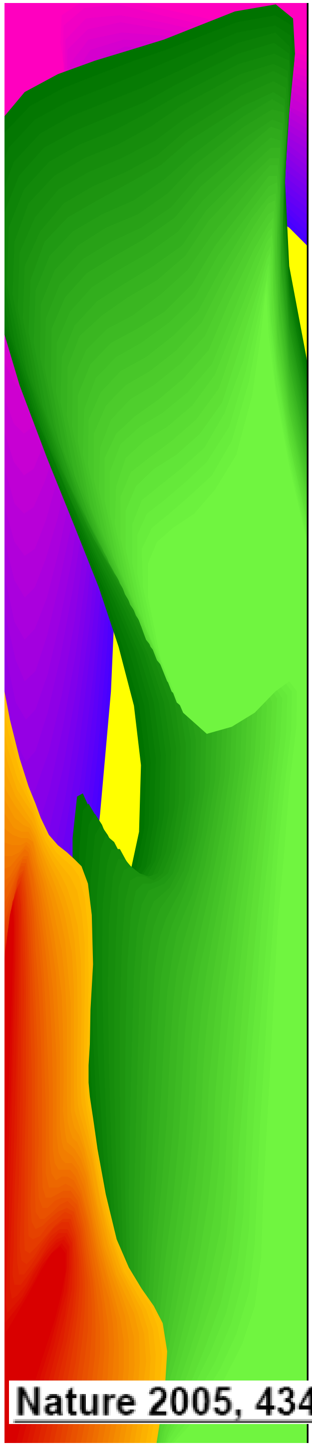








http://www.iapp.de/orgworld



Nature 2005, 434, 194

Conjugated polymers

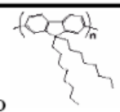
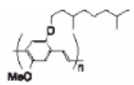
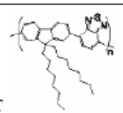
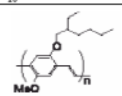
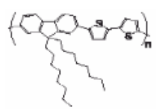
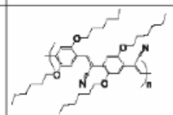
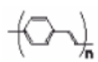
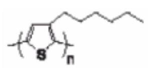
- high charge carrier mobilities, prepared from solutions
- outstanding optical features in the UV Vis region
- poly(acetylene)s, poly(pyrrole)s, poly(thiophene)s, poly(aniline)s, poly(fluorene)s, poly(p-phenylene sulfide), poly(p-phenylene-vinylene)s …

mechanical flexibility, low molecular weight,low-cost manufacturing

Flexibility of properties: modifications by chemical synthesis and deposition and post-deposition techniques

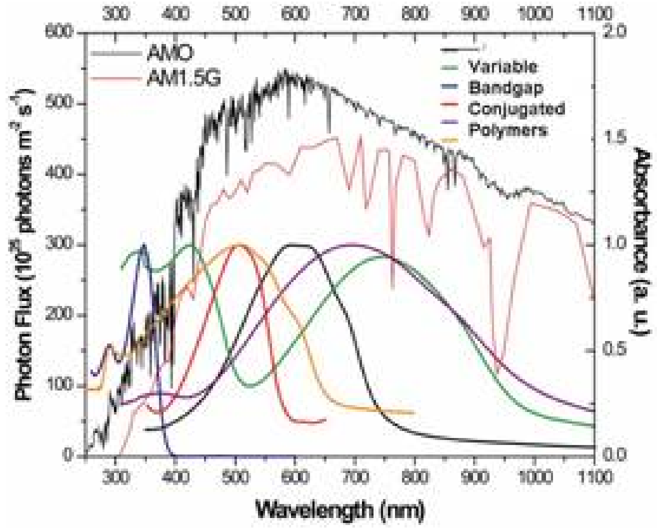
Relatively strong absorption ($\alpha \sim 10^4 \sim 10^5$ cm^{-1})

HOMO / LUMO (eV) Hole / Electron mobility ($cm^2V^{-1}S^{-1}$)

 PFO	5.7 / 2.4 $3X10^{-4}$ / $5X10^{-3}$	 OCC_{10}-PPV	5.0 / 2.8 $5X10^{-4}$ / $8X10^{-5}$
 F8BT	5.9 / 3.3 NA / $4X10^{-3}$	 MEH-PPV	5.0 / 2.8 $5X10^{-5}$ / $3X10^{-5}$
 F8T2	5.5 / 3.1 $5X10^{-3}$ / $6X10^{-3}$	 CN-PPV	5.4 / 3.2 NA / $4X10^{-5}$
 PPV	5.2 / 2.7 NA / $1X10^{-4}$	 P3HT	4.9 / 2.7 $2X10^{-4}$ / $6X10^{-4}$

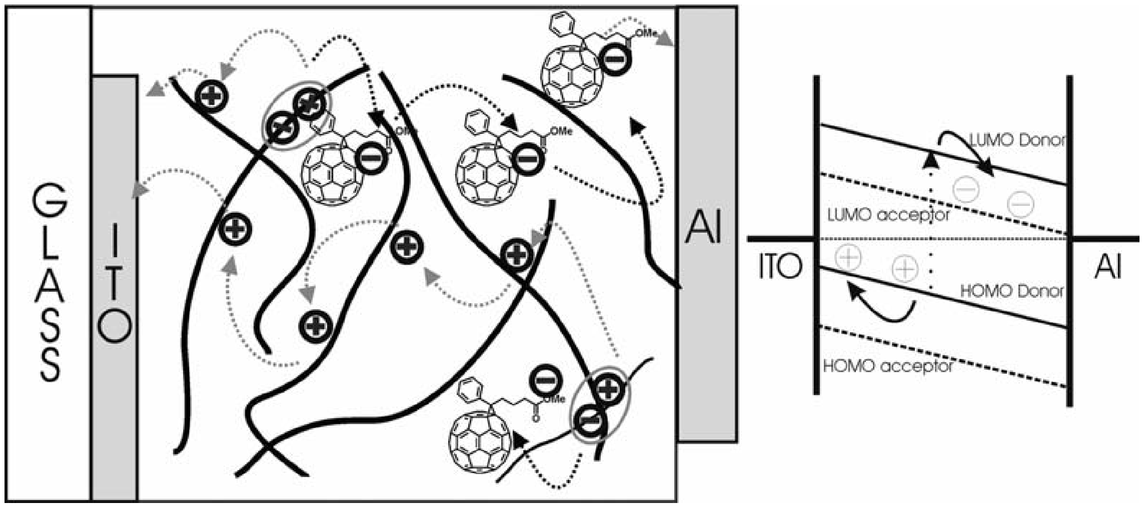
Conjugated polymers devices

Major issues:
1. nano-morphology optimization
2. improving charge carrier mobility
3. improving spectral sensitivity



Variable band gap: by the design and synthesis (1.5 - 2.3 eV) HOMO/LUMO electronic energy levels modulated as desired

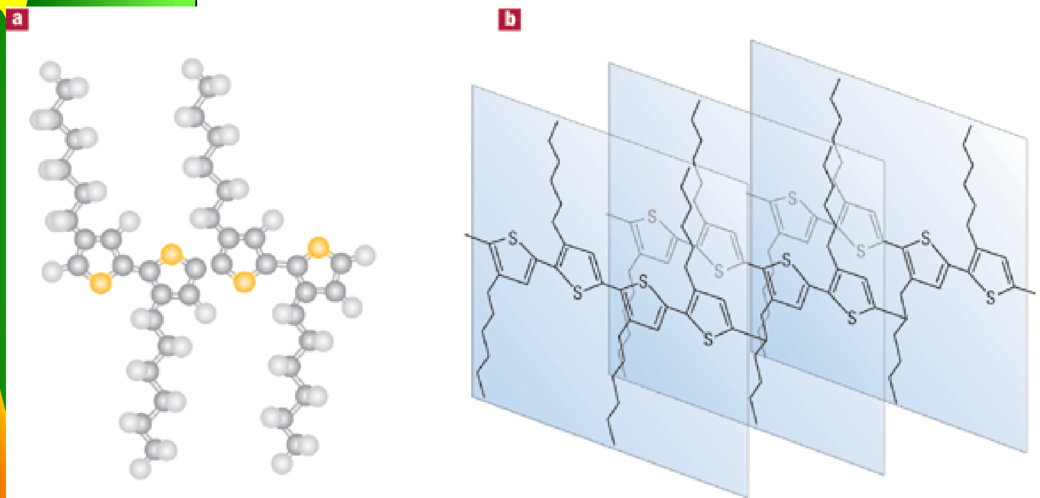
www.chem.ufl.edu/~reynolds/research/pages/pho...



A.J. Mozer, N.S. Sariciftci / C. R. Chimie 9 (2006) 568–577

p-type organics: P3HT

- poly(3-hexylthiophene) = donor type semiconductor
- high ordering-induced mobility
- an improved solar-spectrum absorption up to 650 nm, absorption onsets at ~ 2 eV
- one of the most widely studied class of soluble semiconducting polymers
- the rings contain four carbon and one sulphur atom
- the stacking of polythiophene molecules into an ordered lamella

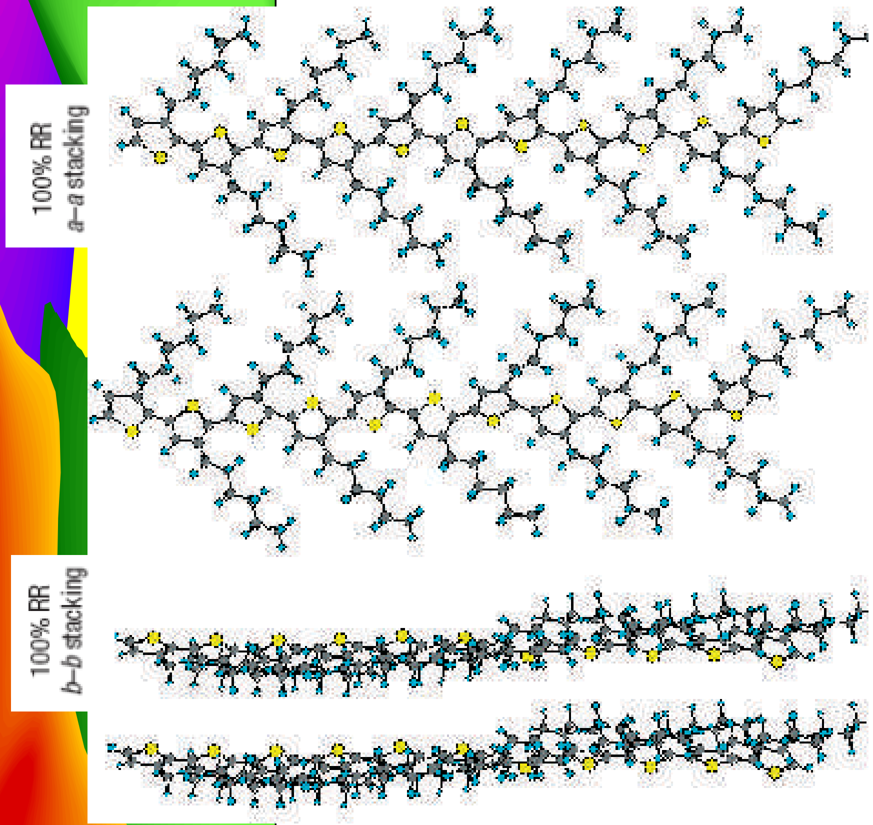


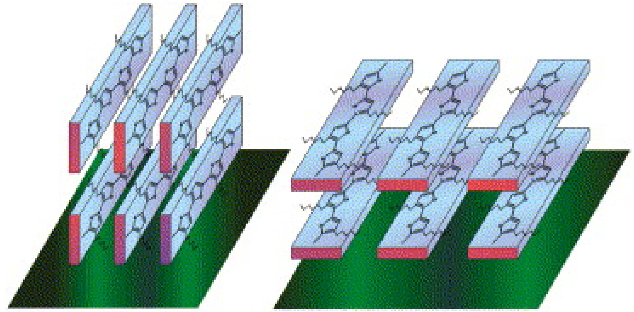
www.nature.com/.../n3/fig_tab/nmat1601_f1.html

J.A. Koster, University of Groeningen

Regioregular P3HT stacking

Variations in RR … distinctly different orientations relative to the substrate





RR = strong h-t, h-h or t-t coupling (regiorandom – statistical coupling)
RR = enabling **closer packing** of the lamellae to the substrate
2-dimensional lamellar structure
Optical (and electrical) excitations adopt some **interchain character** responsible for a distinct shoulder on the long wavelength side of the absorption maximum

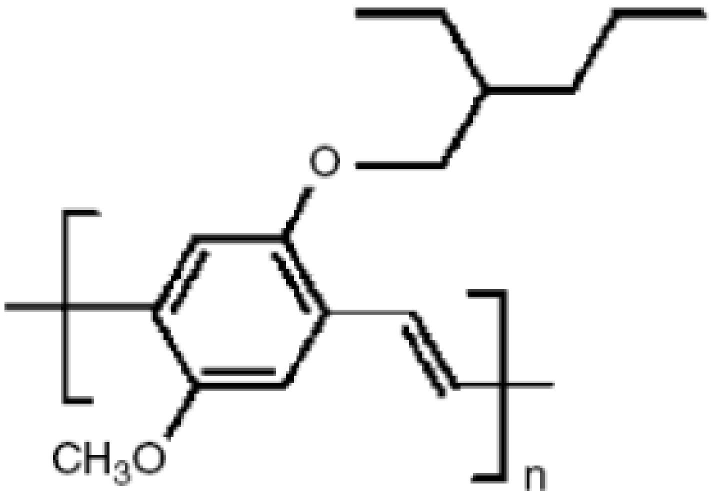
Youngkyoo Kim *et al*., Nature Materials, vol. 5 2006, 197

MEH-PPV

- poly(2-methoxy, 5-(2-ethyl-hexyloxy)-1,2-phenylene-vinylene)
- important member of PPV family, dialkoxy derivative of PPV, phenyl ring, C-O bonds
- excelent processibility, favourable optical and electronic properties
- one of the highest conversion efficiency, absorption onsets at ~ 2.1 eV

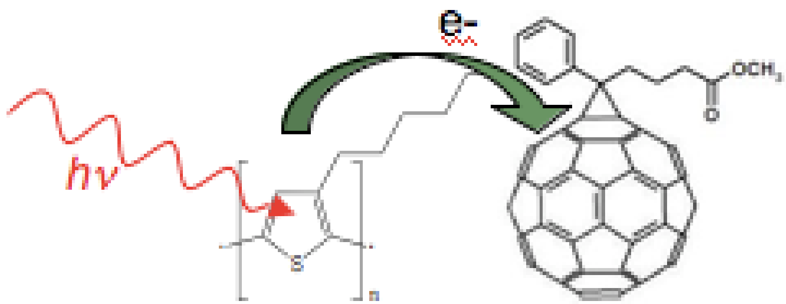
MEH-PPV LED

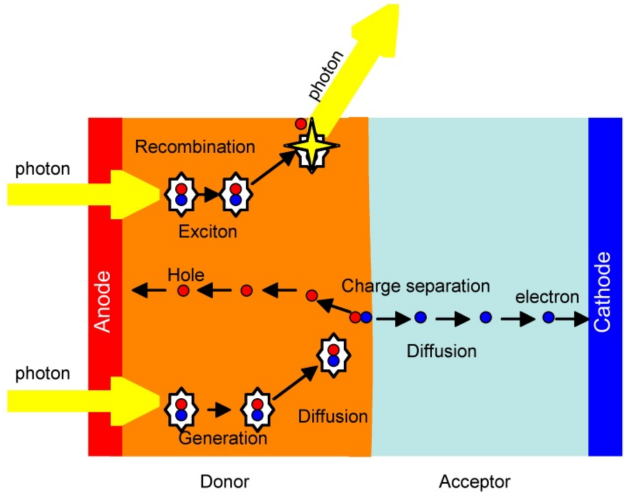
physics.ucsc.edu/~sacarter/polymers.shtml



MEH-PPV

Organic solar cells





T. Kietzke, *Adv. OptoElectron.*, 2007, 40285, 1

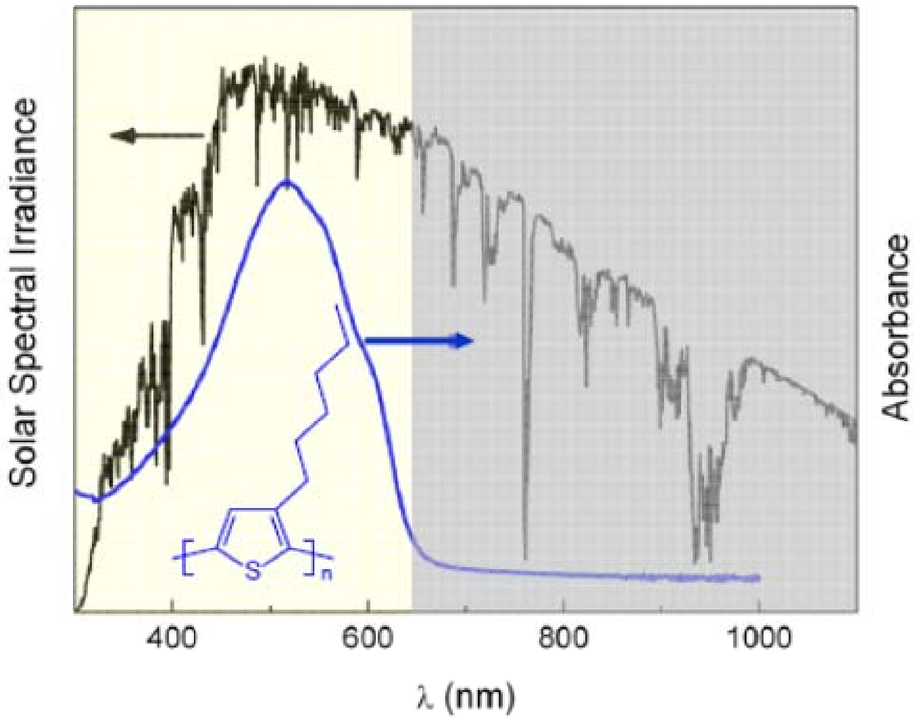
Fundamental steps of the PV process in systems having deloxalized π-electrons:

1. Absorption of sunlight and generation of **excitons**
2. **Diffusion** of excitons and their dissociation with generation of **free charge carriers**
3. Transport and **collection** of charge carriers

BHJ solar cells

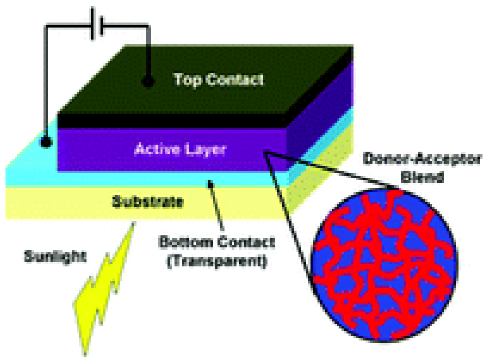
Current state of art: power efficiencies of P3HT:PCBM BHJ solar cells between 5% and 6% (5% certified by NREL)

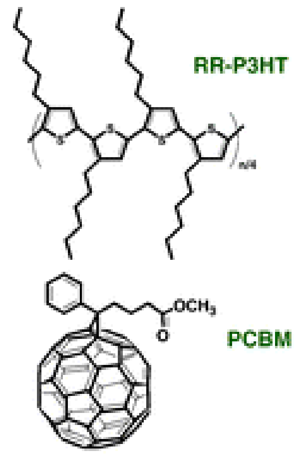
Bulk heterojunction architecture of solar cells: blends of electron donating and electron accepting materials
P3HT:PCBM … the most efficient organic blend (efficiency as high as ~ 5 %)



PV conversion originates directly from P3HT absorption

Limiting factor: only 23% of the photons of the AM 1.5 spectrum can be absorbed by P3HT !



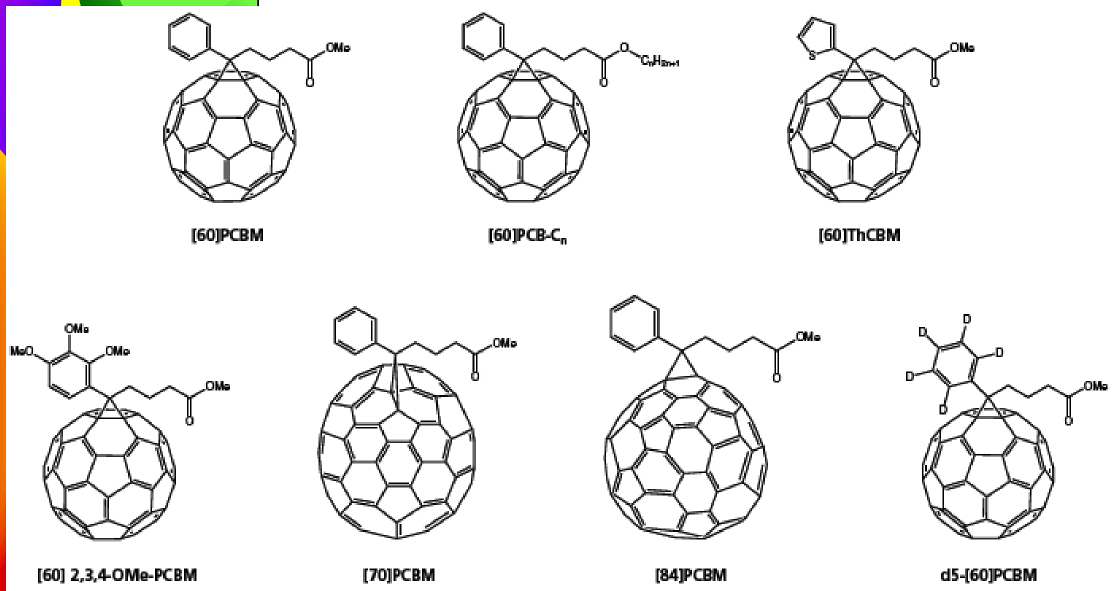


N. Camaioni, Workshop on Nanoscience for Solar Energy Conversion, 2008

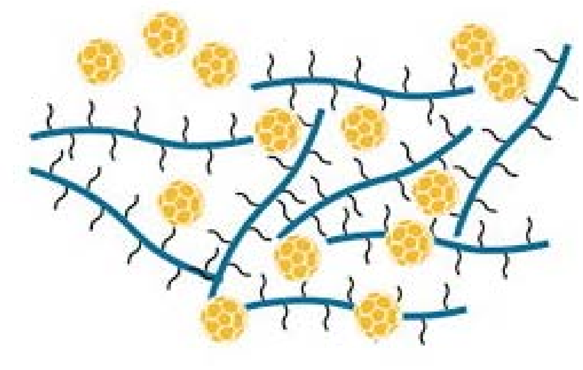
G. Li, V. Shrotriya, Y. Yao, J. Huang, Y. Yang, *J. Mater. Chem.*, Vol. 17, 3126 (2007)

n-type organics: fullerenes

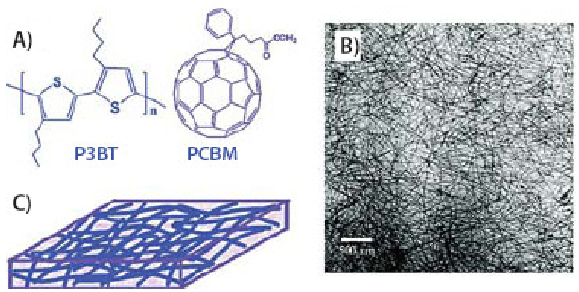
- PCBM … effective organic n-type semiconductor
- Metallofullerene (**P**henyl - **C**$_{61}$ – **B**utyric – Acid – **M**ethyl -Ester)
- Rich library of PCBMs (60PCBM analogues)
- Excellent electron accepting and transporting properties, limited ability to absorb visible light



David Kronholm, Jan C. Hummelen Material Matters 2007, 2.3, 16



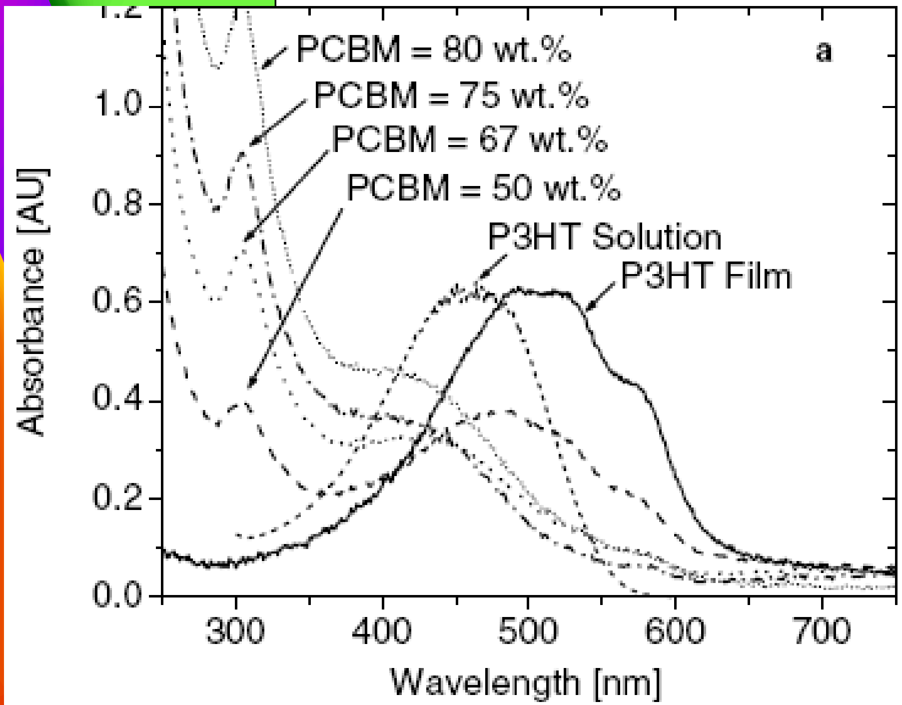
Mitch Jacoby, adapted from J.Phys.Chem.Lett.

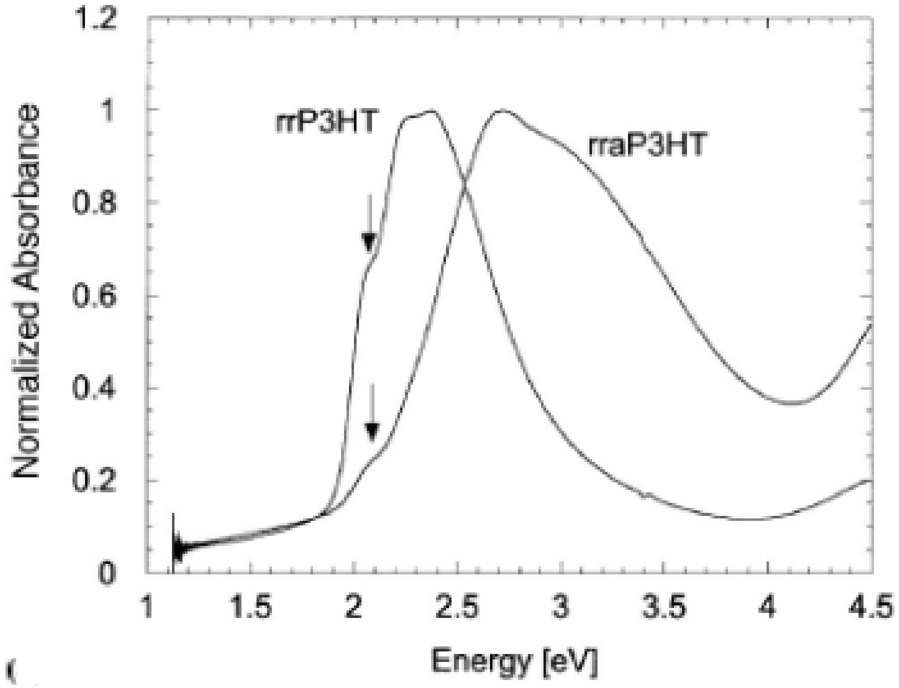


Nicholas S. Colella, Lei Zhang, Alejandro L. Briseño, Material Matters - Volume 7, Number 1

Absorption in P3HT:PCBM

Optical and electrical properties of P3HT: sensitive to molecular packing in pristine P3HT as well as in P3HT/PCBM blends (for BHJ solar cells)



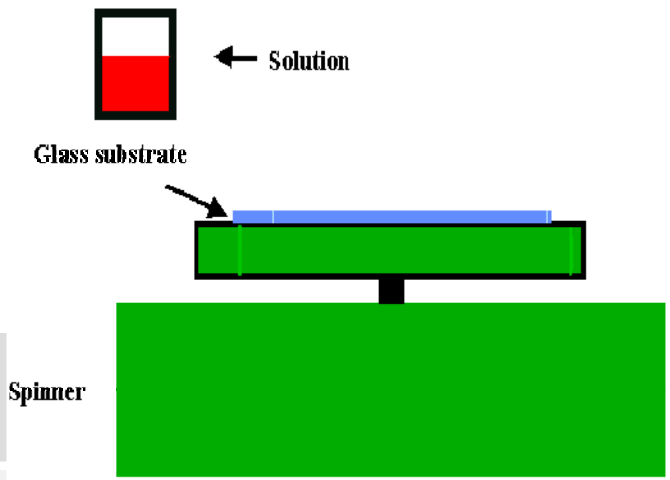


P.J. Brown *et al.*, Phys. Rev. B 67, 064203 (2003)

V. Shrotriya *et al.*: Chemical Physics Letters, Vol. 411, 138 (2005)

Research on P3HT:PCBM

- **Institute of Physics, Slovak Academy of Sciences, Bratislava, Dr. V. Nádaždy**
- Electronic grade RR P3HT (Sigma-Aldrich), rr > 98 %
- PCBM (Sigma-Aldrich), purity > 99.5%
- P3HT:PCBM blends prepared in dichlorobenzene with concentration of 2 wt %
- Spin-coated on cleaned (ultrasonically in acetone and isopropanol and UV irradiated) ITO substrates
- solvent annealed in Petri dish with *Φ*= 9 cm for 20 min
- thermal annealing at 110 ^{o}C for 4 min in Ar atmosphere
- the thickness of the samples ~ Dektak profilometer

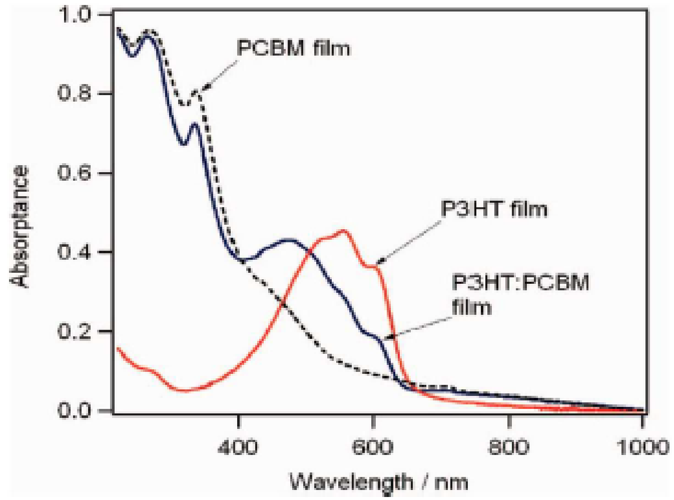


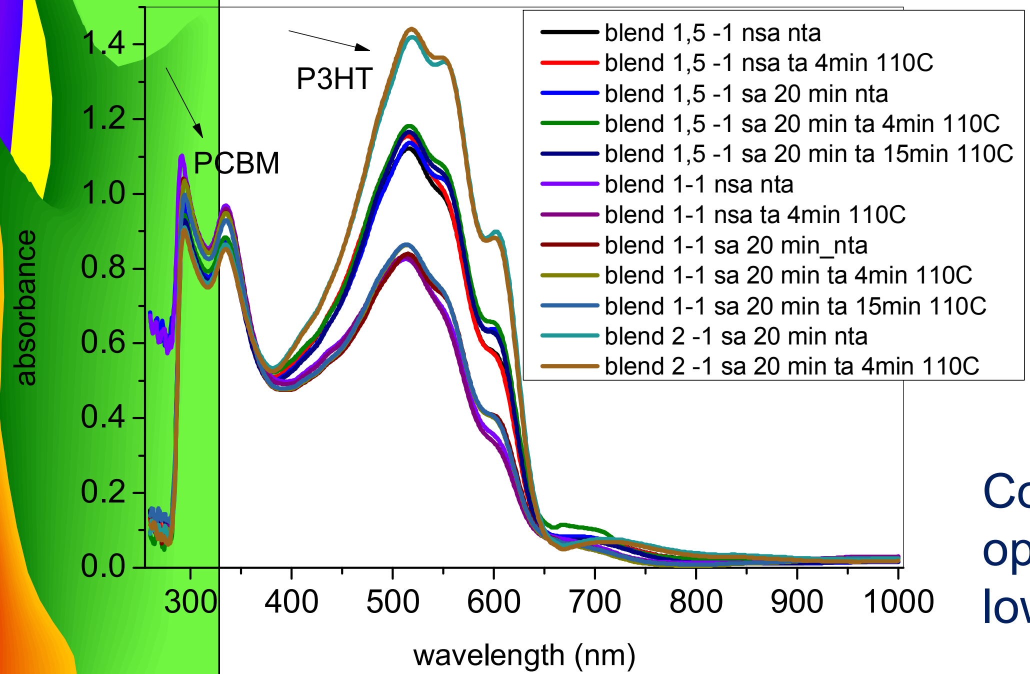
Sample notification	[P3HT:PCBM] blends ratios	Thermal annealing	Spin coating	Thickness (nm)
1.5:1nta	1.5:1	no	20 rps, 70 s	263
1.5:1ta	1.5:1	4 min 110° C	16 rps, 100 s	168
2:1nta	2:1	no	20 rps, 70 s	307
2:1ta	2:1	4 min 110° C	16 rps, 100 s	171

›ptoweb.fis.uniroma2.it/opto/ormosil/spin.html

Absorption spectra

- Shimadzu UV-Vis-NIR spectrophotometer in the double beam operation with ITO substrate as a reference
- To avoid the thickness dependence of absorbance, absorption coefficients calculated and background subtracted





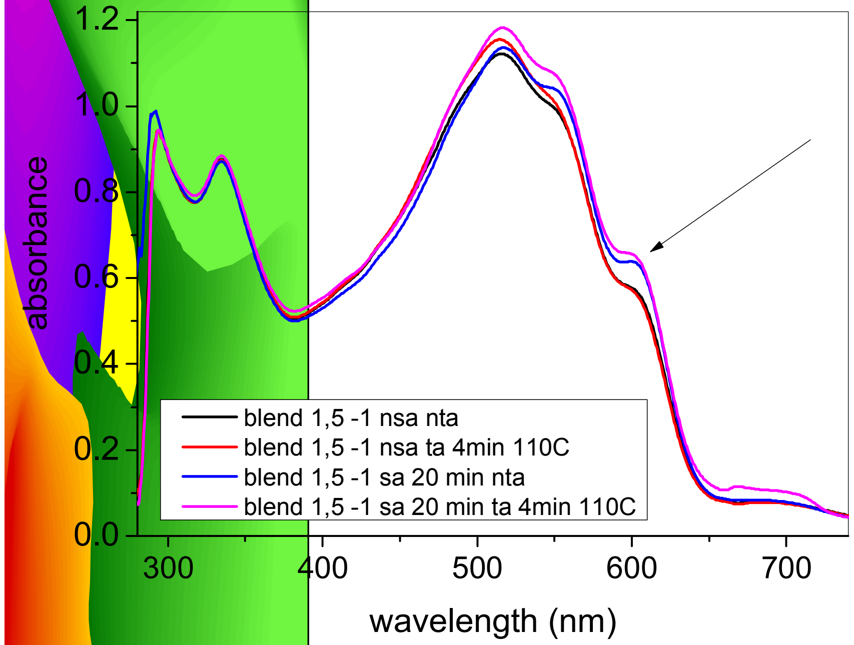
Absorption broadening in conjugated polymers arises from coupling between conjugated segments and from characteristic distribution of conjugation lengths

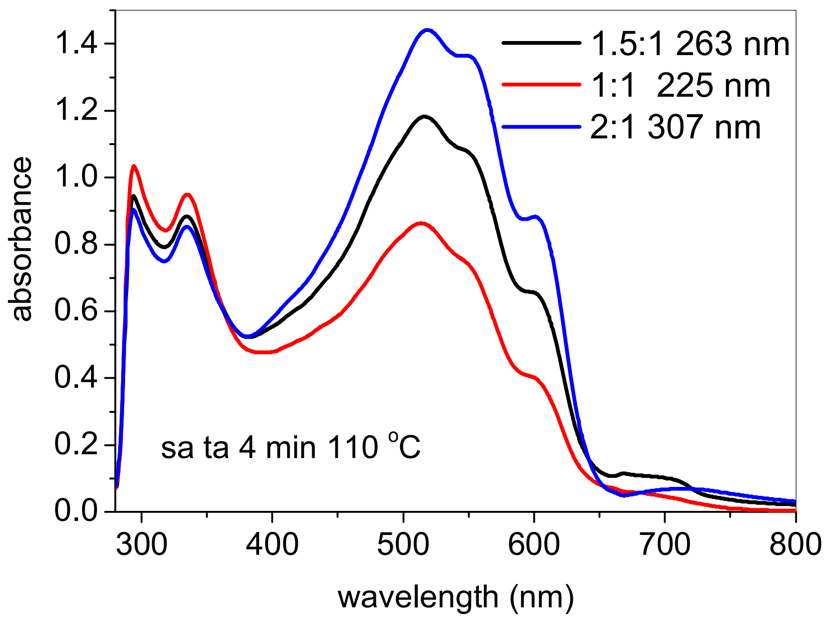
Correlation to BHJ solar cell operation=> nsa nta blends = much lower efficiencies

S. Cook, R. Katoh, A. Furrube, J. Chem. Phys.C 113, 2009, 2547

Solvent annealing & blend ratio

Solvent annealed samples – more pronounced shoulder at ~ 600 nm





Correlation to BHJ solar cell operation=> sa blends = higher efficiencies

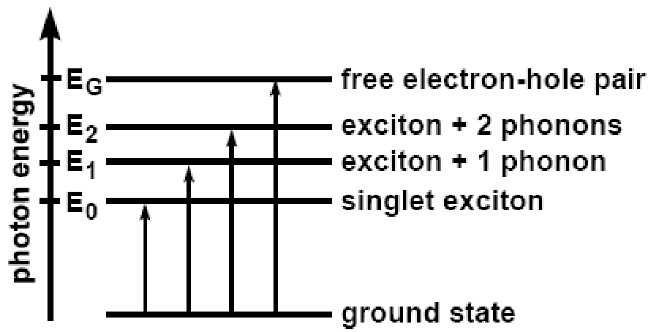
Optimal blend ratio … 1.5:1 ÷ 2:1

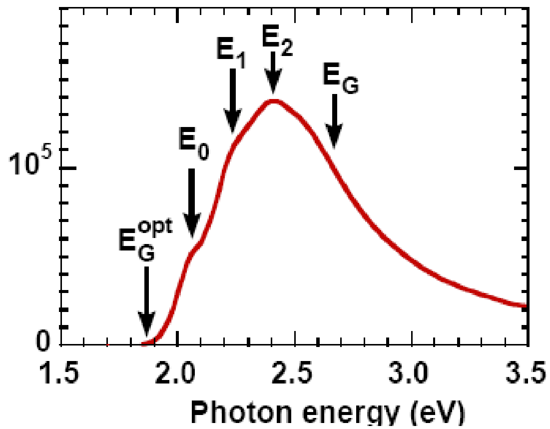
Resolved features of structured absorption

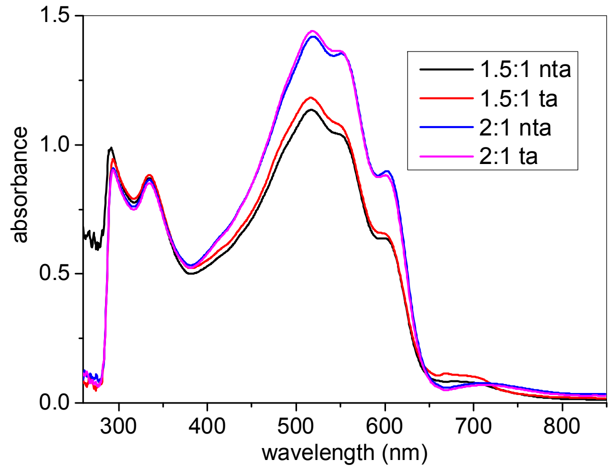
Exciton …bound pair of electron and hole
Effective exciton generation mostly occurs in donor-rich material

Pristine P3HT	E_g	E_2	E_1	E_0
Wavelength [nm]	~ 480	~ 515	~ 560	~ 605
Photon energy [nm]	~ 2.60	~ 2.40	~ 2.20	~ 2.05
Assignment	band-to-band	exciton+2 phonons	exciton+1 phonon	singlet exciton

- upon light an exciton is created, not free charge carriers !
- excitonic features broadened by electron-phonon (vibronic) coupling,



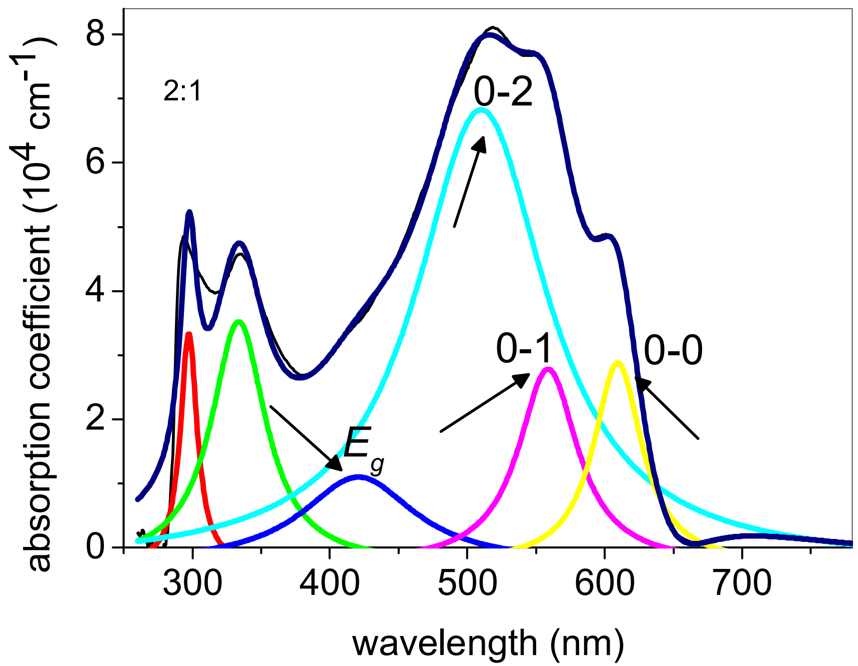




Spectra decomposition

Integrated total blend absorption:
after thermal annealing increases by ~1.8 times in comparison with non-thermally annealed blends under the same other conditions

Pronounced excitonic peaks = indicating **a certain degree of ordering.**

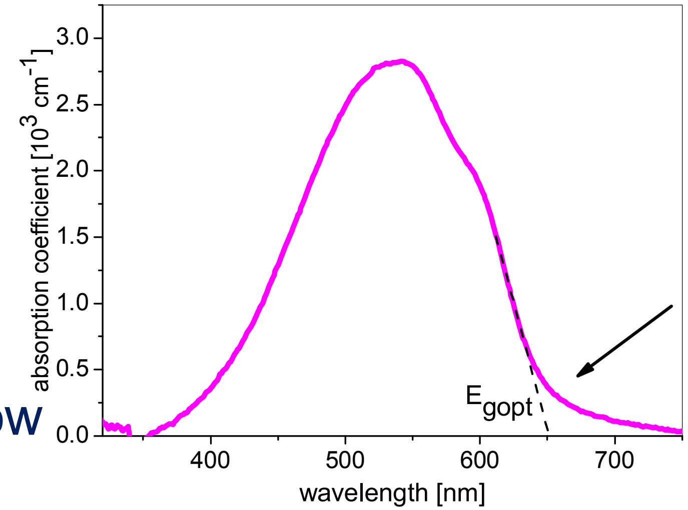


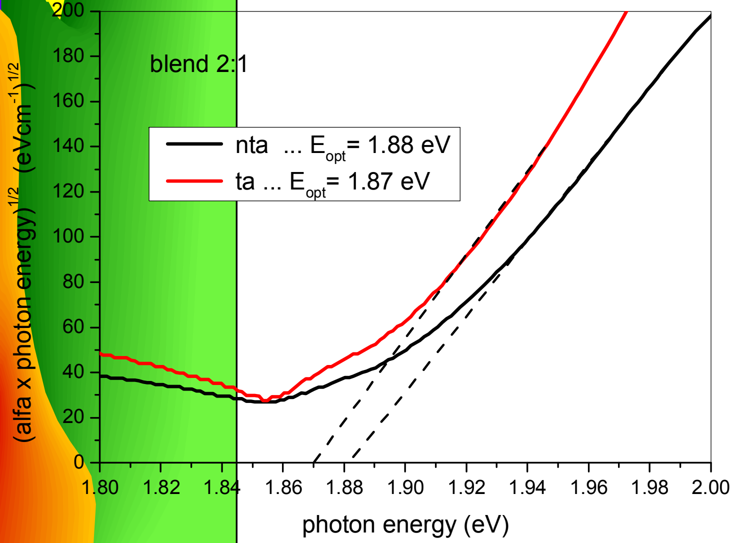
	band-to-band	exciton+2 phonons	exciton+1 phonon	singlet exciton
Assignment	E_g	**0-2**	**0-1**	**0-0**
Absorption peak [eV] 1.5:1 nta	2.93	2.43	2.22	2.03
Absorption peak [eV] 1.5:1 ta	2.95	2.43	2.22	2.03
Absorption peak [eV] 2:1 nta	2.97	2.42	2.22	2.04
Absorption peak [eV] 2:1 ta	2.93	2.43	2.22	2.03

Optical band gaps

The absorption peak positions and optical band gaps depend on the conjugation length of polymer chains and intra-chain interactions.

The optical band gaps - the intersection of the tangent on the low energetic edge of the absorption spectrum with the abscissa (Tauc plot)





~ 1.87 eV for the annealed blends
~ 1.88 eV for the non-annealed blends

No specific dependence on the P3HT:PCBM ratio and post-deposition treatment was detected.

Absorption vs.morphology

A model by F.C. Spano*: intensities of individual transitions are widely affected by the exciton bandwidth W

$$A(E) \propto \sum_{m=0} \left(\frac{S^m}{m!}\right) \times \left(1 - \frac{We^{-S}}{2E_p} \sum_{n \neq m} \frac{S^n}{n!\, n-(m)}\right)^2$$

$$\times \exp\left(\frac{\left(E - E_{0-0} - mE_p - {}^1\!/_2 WS^m e^{-S}\right)^2}{2\sigma^2}\right),$$

- E_p ~ 0.18 eV … phonon energy of the main oscillator coupled to the electronic transition
- refractive index ratio ~ 0.98

  The free exciton bandwidth W ~ inversely proportional to the conjugation length (and propotional to high excitonic coupling)

  Change of conjugation length with aggregation

- E_p ~ 0.18 eV … phonon energy of the main oscillator coupled to the electronic transition
- refractive index ratio ~ 0.98

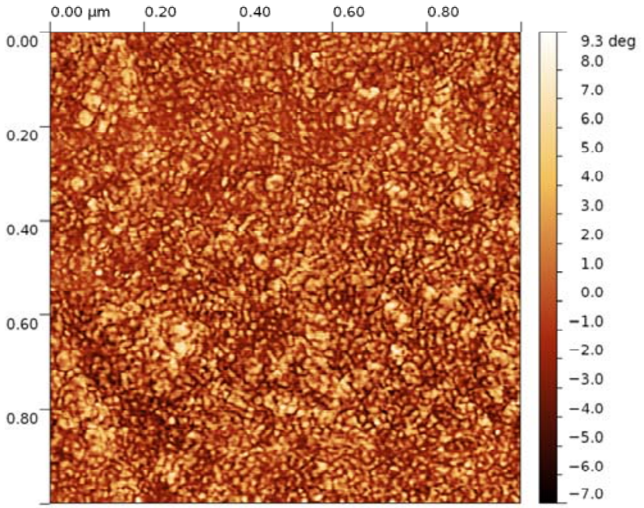
- Increase of W = an indication of the presence of shorter conjugated segments
- No special behavior connected with the blend ratios observed

F. C. Spano, *J. Chem. Phys.*, 2005, 122, 234701

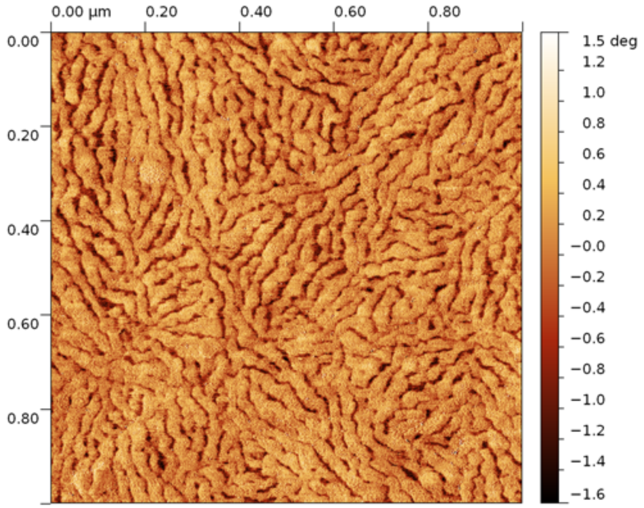
F.C. Spano, *J. Chem. Phys.*, 2006, 325, 22

Blend morphology optimization

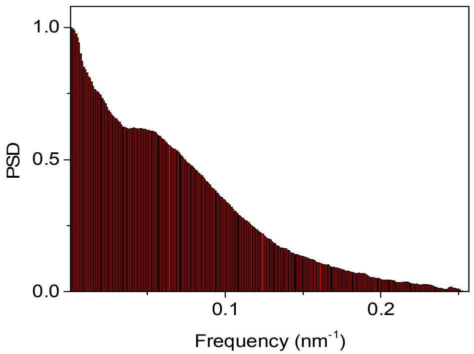
Before solvent and thermal annealing

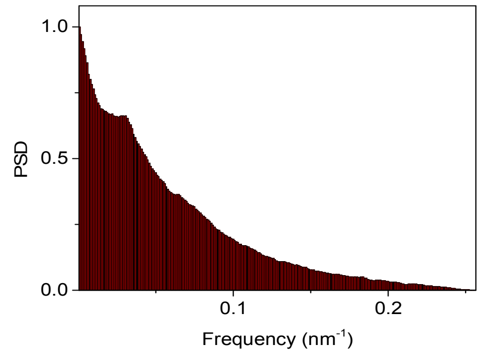


After



Power spectral density versus spatial frequency:





After thermal annealing – the length of interacting P3HT chains increases

Exciton diffusion length ~10 nm to diffuse to donor-acceptor interfaces

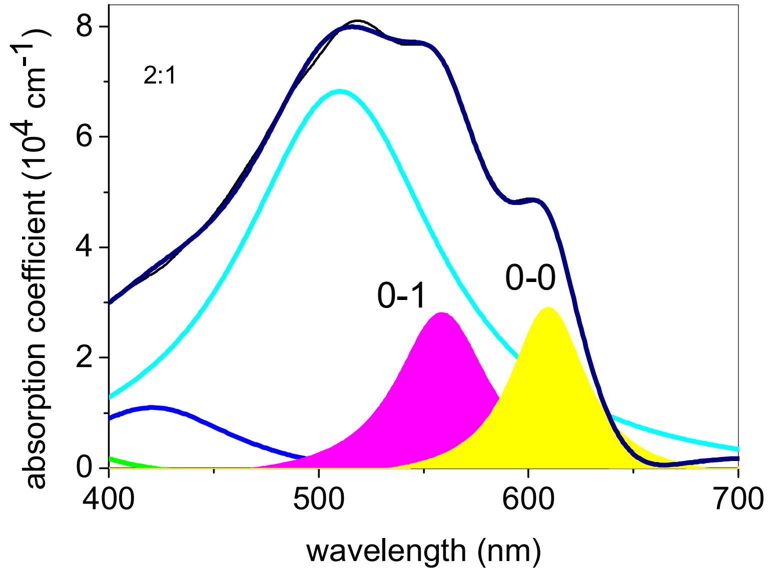
By courtesy of Dr. Jergel and Dr. Halahovets, IP SAS:

AFM tapping phase contrast image

Free exciton bandwidth

The ratio of absorbances in vibronic 0-0 and 0-1 peaks = an indicator of the intermolecular coupling energy.

$$\frac{\alpha_{0-0}}{\alpha_{0-1}} \approx \frac{n_{0-1}}{n_{0-0}}\left(\frac{1-0.24W/E_p}{1+0{,}073W/E_p}\right)^2$$



Sample	1.5:1 nta	1.5:1 ta	2:1 nta	2:1 ta
W (meV)	41	110	31	121

- Increase of *W* = an indication of the presence of shorter conjugated segments => increase in absorption
- No special behavior connected with the blend ratios observed => PCBM plays little role in the formation of P3HT morphology

J. Clark, C. Silva, R.H. Friend, F. C. Spano, *Phys. Rev. Lett.*, 98, 206406-1 – 206406-4 (2007)

Research on post-deposition processing

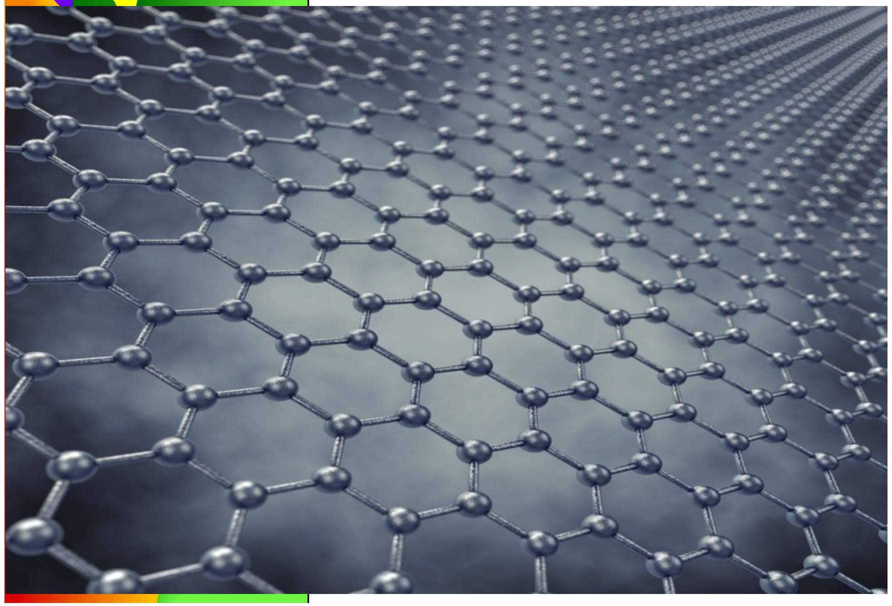
- The solvent and thermally annealed samples showed higher absorption and higher free exciton bandwidths (increased efficiencies of solar cells).

- We deduce that increased absorption is due to chain ordering after thermal annealing enabling more effective light harvesting and charge carrier formation in photovoltaic devices.

- Strong interchain interaction may cause the increase of carrier mobility.

Graphene

- promising class of organic semiconductors, **discovery announced in 2004 by Science**
- atoms arranged into a 2D honeycomb structure
- one of the simplest graphenes = HBC-$C_{12}H_{25}$ (HBC)
- HBC's disk like molecules easily form 2D conducting layers
- columnar self-organization of discotic type with prominent 1D - conducting properties
- high mobility and optical transparency, flexibility, robustness and environmental stability



wired.co.uk, shuttlestock

Several recent results – from solar cells and light-emitting devices to touch screens, photodetectors and ultrafast lasers
Review: *Nature Photonics* 4, 611 - 622 (2010)

J. Wu, W. Pisula, K. Müllen: Chemical Reviews, 20017, 107, 718

Conclusion

Photonics materials = novel physical properties of new or known ones that should be revealed

Photonics = interaction of light and matter for:

- applications
- characterization