CHEM 524 Course Outline (Sect. 4) – 2013

For html Version of This Set of Notes with Linked Figures from 2005 CLICK HERE

Text: Chapter 3, Sect 1 and 4,5 directly relates to lecture, in good depth – optics do not change

III. Optics — Control of light — goal: move radiation from the source to the detector in a controlled manner through the experiment

A. Lenses + Mirror (Text: Ch 3 & 1,4) design — shape & materials — efficiency

1.Basic concepts:

index of refraction — **n = c/v**, c = 3 x 10^8m/s, in a material, the speed of light is reduced < c

n_{CaF2} ~ 1.35, n_{ZnSe} ~ 2.5, n_{Ge} ~ 4 ($n_{fus.qtz}$ ~ 1.458, glass: crown~1.57, flint~1.65, pyrex ~1.47)

[silicates: crown - ~10% KO or other oxides, flint - original had PbO, now TiO or ZrO, pyrex- B_2O_3]

– index goes up with absorbance and delocalization of electrons (heavy atoms, π-systems)

– liquids as well: n_{water} ~ 1.33 , $n_{alcohol}$ ~ 1.36, n_{CCl4} ~ 1.466, $n_{Br\text{-}napthalene}$ ~ 1.659

non-isotropic (bi-refringence) depends on direction:

quartz (SiO_2): n_o ~ 1.544 n_e ~ 1.553, calcite ($CaCO_3$): n_o ~ 1.6557 n_e ~ 1.4852, zircon ($ZrSiO_4$): n_o ~ 1.923 n_e ~ 1.968 , MgF_2: n_o ~ 1.390 n_e ~ 1.378, TiO_2: n_o ~ 2.583 n_e ~ 2.865

CdS : n_o ~ 2.281 n_e ~ 2.297 , CdSe: n_o ~ 2.46 n_e ~ 2.48 (λ=2.5 μm)

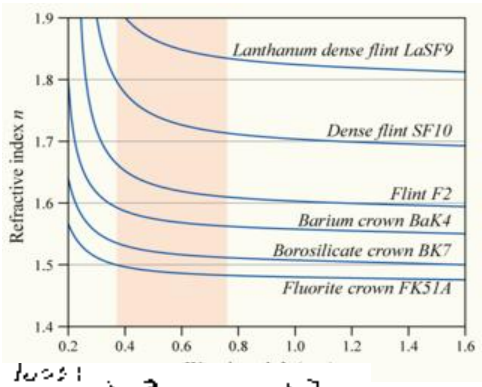
(*uniaxial* crystals, o = ordinary, xx and yy, e = extraordinary, zz) – contrast cubic xtal only n

conservation law: **ρ(λ) + α(λ) + T(λ) = 1** – (do not lose light) mirror T~ 0 & lens T ~ 1

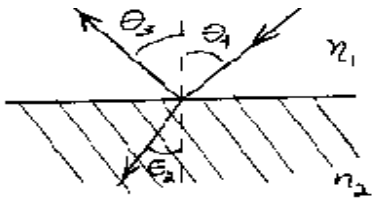
dispersion (index, n, short λ, increase with decrease in λ)

— dn(λ)/dλ < 0 -- bend light by color

(typical: decrease with increased wavelength λ,
exception, if absorption band, *index is complex* and has singularity, derivative shape, -/+ as inc. λ)



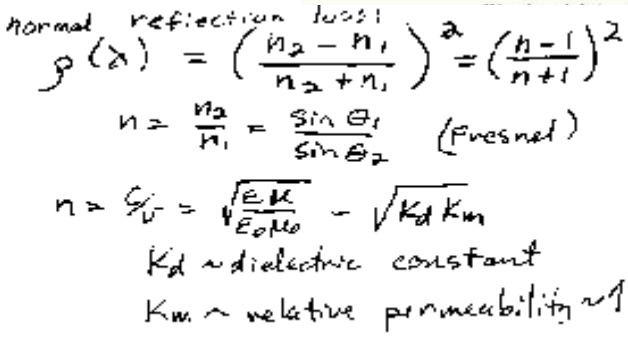
Snell's law of refraction: **$n_1 \sin\theta_1 = n_2 \sin\theta_2$,**



$\theta_1 = \theta_3$ - specular reflection

$\theta_2 < \theta_1$ if $n_1 < n_2$

$n_1 \sin\theta_1 = n_2 \sin\theta_2$



reflection: $\theta_1 = \theta_3$ vs. refraction: $\theta_2 < \theta_1$ for $n_1 < n_2$ – low → high, beam toward normal

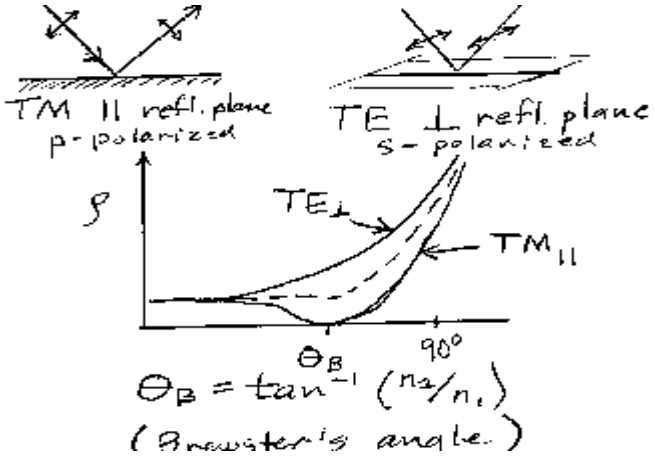
reflection loss: $\rho(\lambda) = (n_2-n_1)^2/(n_2+n_1)^2$, normal incidence, *more at angle* (window→mirror)

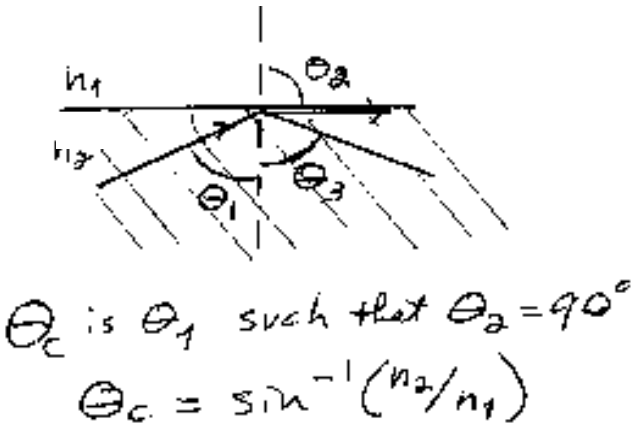
e.g. air/glass ~ 4% - i.e.$[(1.5-1.0)^2/(1.5+1.0)^2 \sim 0.2^2 = 0.04]$, but ZnSe ~18% per surface

Brewster angle, — zero reflection loss in one polarization (II to reflection plane)

at specific angle $\theta_B = \tan^{-1}(n_2/n_1)$ - other polarization, **||** *surface, always some loss*

general: transmit plus reflection, due to interface, always loss, but also shift polarization

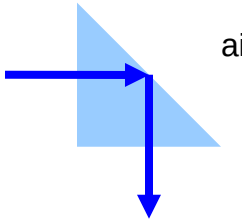




ex: **Brewster** - *air-glass:* $\tan^{-1}(1.5/1) = 56.3^o = \theta_B$ **Critical angle**: $\sin^{-1}(1.0/1.5) = 41.8^o = \theta_c$

- note: θ_B most useful for $n_2 > n_1$ *but θ_c only for $n_1 > n_2$*

Total internal reflection, - critical angle - **for $n_1 > n_2$,** $\rho(\lambda)$ max at $\theta_1=\theta_c$, $\theta_c = \sin^{-1}(n_2/n_1)$



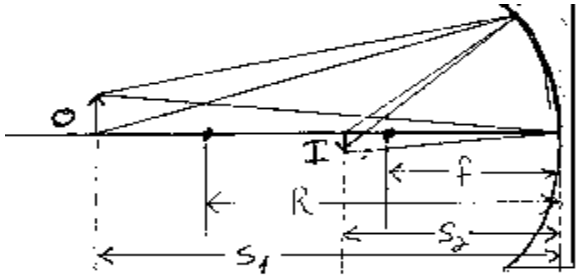
air — glass (or quartz), $\theta_c \sim 42^o$, useful property for prism reflectors

(no coating, higher power possible – useful for steering laser beams)

example: $\theta \sim 45^o > 42^o$ so no transmission, all reflected, *no coating*

but beam must be collimated, or controlled, since angle >42°

2. Mirrors: spherical mirror imaging — reflection,



$1/S_1 + 1/S_2 = -2/R = 1/f$

$R < 0$ — concave

$m = -I/O = -S_2/S_1$

spherical mirror focusing - *mirror formula*: **$-2/R = 1/S_1 + 1/S_2 = 1/f$**

S_1 — object — O, S_2 — image — I (+ if O side), R — radius (R<0 concave), f — focus

Ex.: S_1 = infinite, parallel beam,→ S_2 = f or $S_1 = S_2 = -R$ → 1:1 imaging

magnification: $m = -I/O = -S_2/S_1$ compute where place O to get I of different size, *(-) means flip I:*

result: **$S_1 > R$** — *demagnify*, **$f < S_1 < R$** — *magnify*, **$S_1 < f$** — *no image* (diverging beam)

materials — typically on a glass substrate (stable) or metal for cooling, ground flat or for focus

coating: Al (uv), Ag (vis), Au (IR), overcoating increases ρ , VUV → MgF_2, vis → SiO, TiO

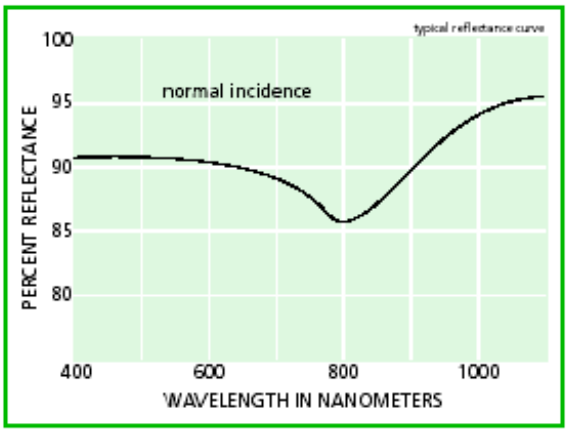


Figure 5.32 **Aluminum coating /016**

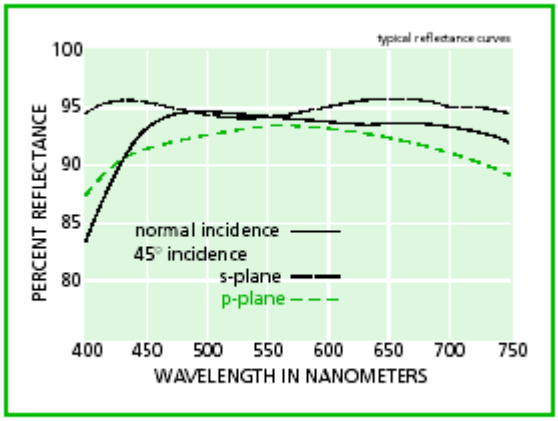


Figure 5.34 **Enhanced aluminum coating /023**

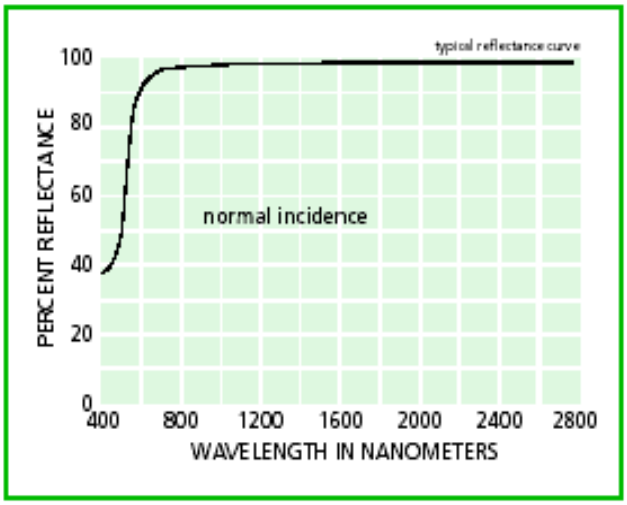


Figure 5.38 **Bare gold coating /045**

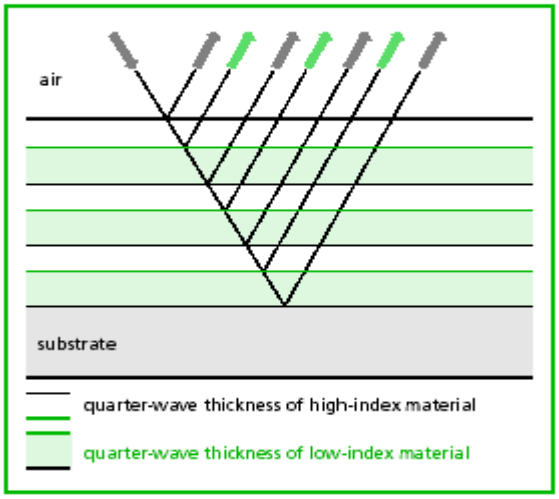
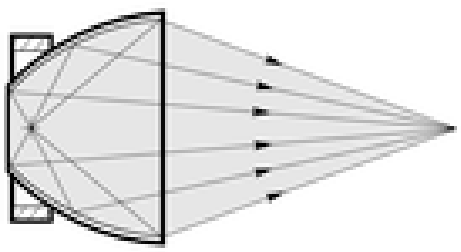


Figure 5.31 **A simple quarter-wave stack**

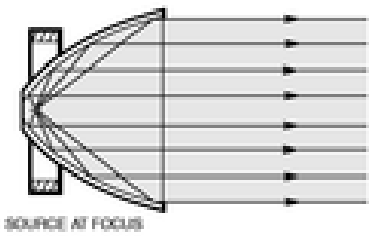
Multilayer dielectric can cause interference (λ/4 reflection out of phase, λ/2 – in phase- increase ρ)

vapor deposit oxides (high n) and fluorides (low n) to get layer effect and internal reflect

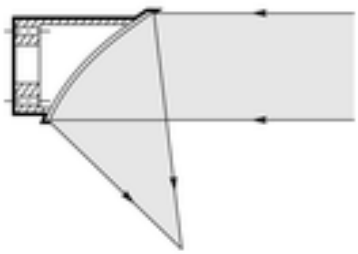
variations: plane, convex (virtual positive image), aspherical, elliptical, parabolic, off-axis parabola



ellipsoidal –refocus

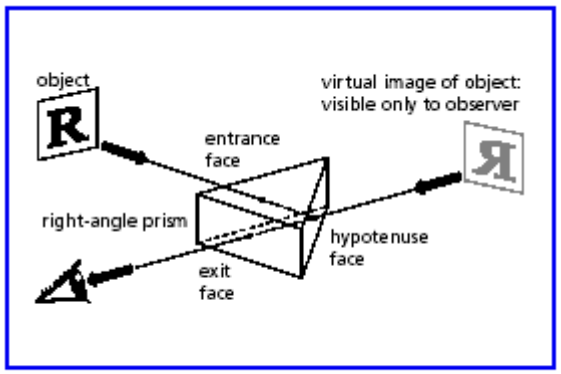


parabaloidal – parallel beam

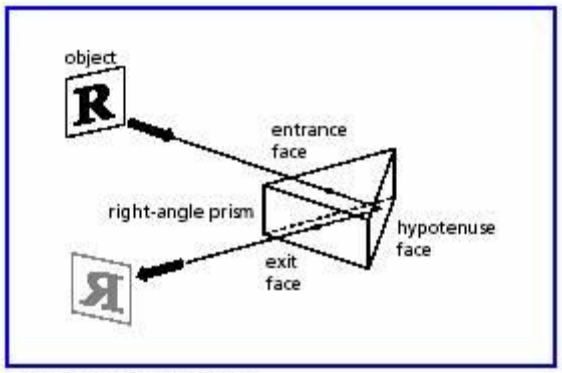


off axis segment

Plane mirror has *virtual image, m = 1*, also for Prism—internal reflection, no coating, high power

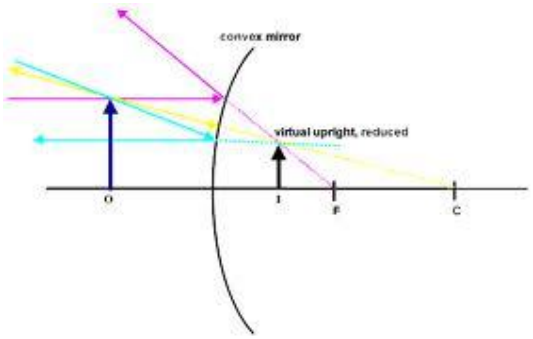


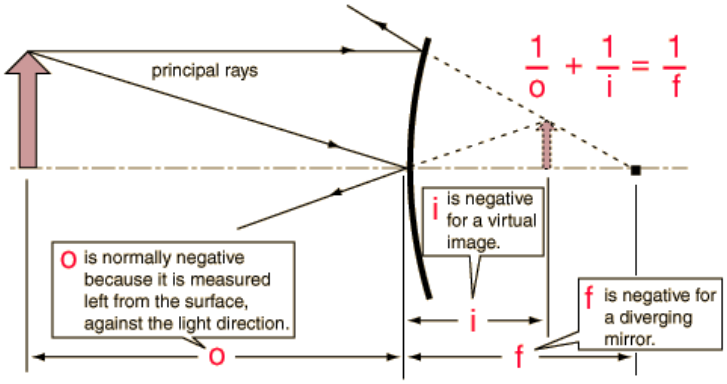
Virtual imaging using a prism



Real imaging using a prism

convex mirror also virtual image but ***m (+),***light diverge from source (object)



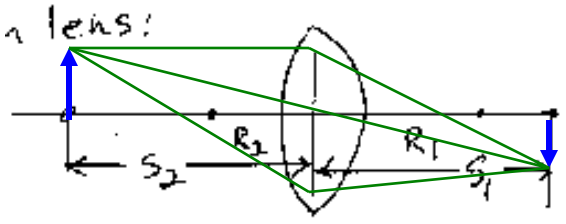


3. Lens: refraction - straight line design, must transmit but losses due reflection or absorption

usable spectral region and focusing range are material and index dependent:

- quartz — uv (180 nm) to near IR ~ 3 μ — 4.5 μ (note absorption band at ~4μ ~2500 cm^{-1})
- CaF_2 — vuv (140+ nm) to mid IR ~ 8 μ -- (BaF_2 goes out to ~12 μ, vuv, ~160+ nm)
- ZnSe — yellow (~500 nm) to IR ~ 16 μ -- (KRS5 –$ThBr_xI_y$ mix – red,~700 nm, to ~25 μ)
- Ge — near IR (~2 μ) to IR ~ 20 μ -- (Si less range ~1.3 to ~16 μ)

Thin-lens model, assume thickness not distort, approximation



$1/S_1 + 1/S_2 = (n-1)(1/R_1 - 1/R_2) = 1/f$

$m = -S_2/S_1$

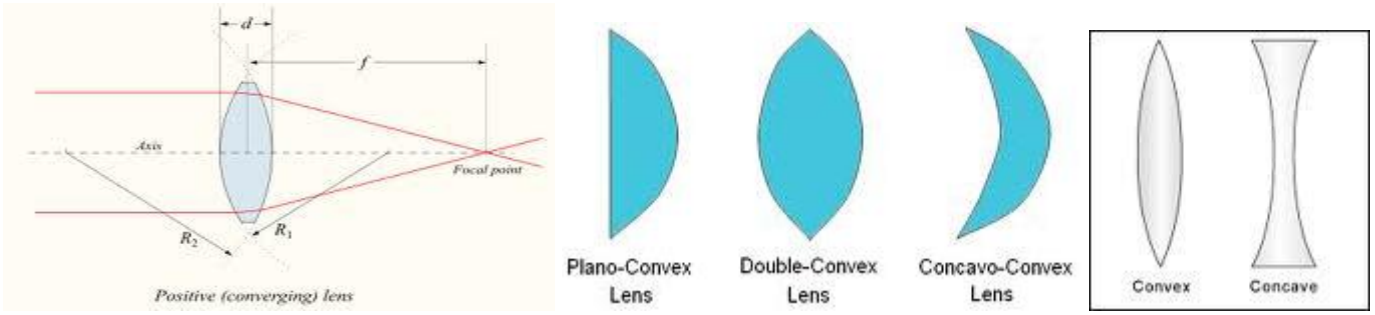
operative formula: **$1/S_1 + 1/S_2 = 1/f$,** from lens makers formula (above)

lens makers formula for one surface: $n_1/S_1 + n_2/S_2 = (n_2 - n_1)/R$, where R is radius of curve

but, typically purchase based on size, focal length, material → *in practice ignore radius*,

but can increase efficiency by choosing best combination

magnification: same as mirror: $m = -S_2/S_1$



special designs: cylindrical (focus 1 dim.), aspherical (reduce aberration), doublets etc. (achromat)

AR coating — reduce reflection loss (n — index lens, n Å 1 air) - $\rho = (n-1/n+1)^2$

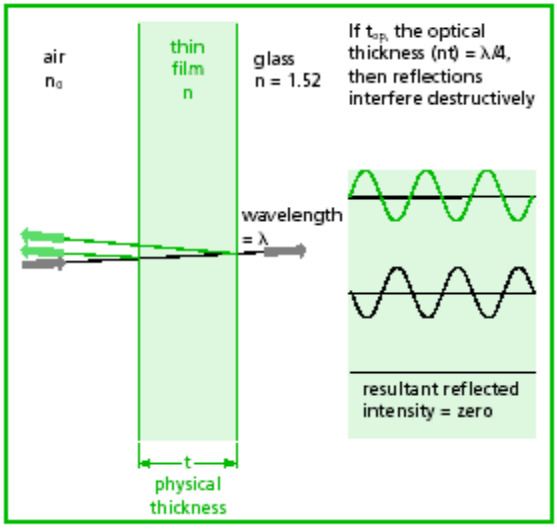


Figure 5.9 **Schematic representation of a single-layer antireflection coating**

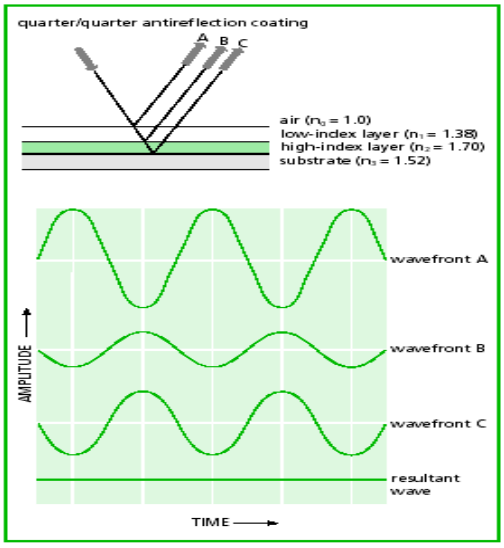
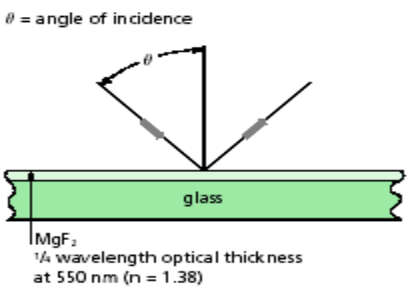
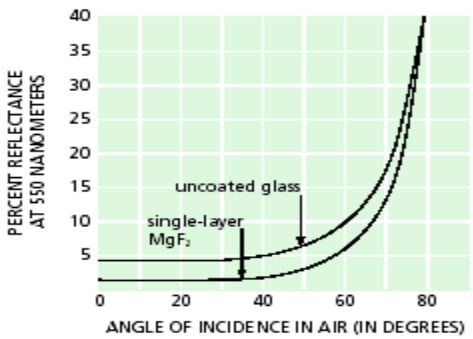


Figure 5.14 **Interference in a typical quarter/quarter coating**

-- add λ/4 layer – intermediate: $1<n_1<n_{sub}$ reflect from 2 surfaces 90^o out of phase - *destructive*

or multiple layers— broaden λ range, goal: zero-out reflect by interference, angle sensitive





-- multilayer (N)— get zeros at (N — 1) λ's – approximate broad band coverage

4. Light gathering power — trade off: more light collect or smaller image spot (m = 1 often best):

closer to source →collect more BUT image bigger
(further, brighter image, smaller spot BUT less light)

F-number: **[F/n] = f/D**, if not circular shape: $D = (4A/\pi)^{1/2}$
Called the speed — *smaller F/n is faster – gather more light*

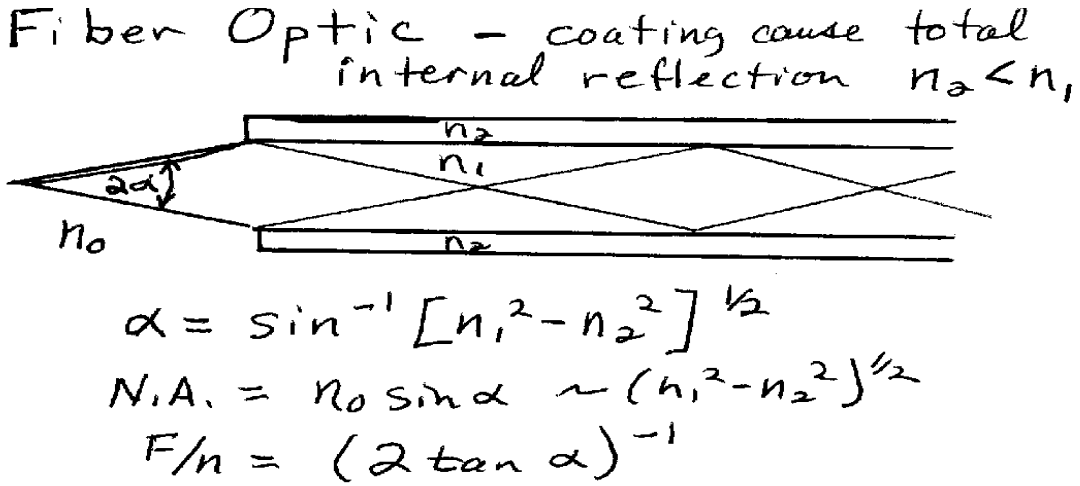
Irradiance (goes as square): halve F/n, quadruple light
(e.g. for photography people: F/1.4 is twice the light of F/2.0)
Varies as solid angle, Ω, $E=B_s(\pi/4)/(F/n)^2$

5. Aberrations (solution):

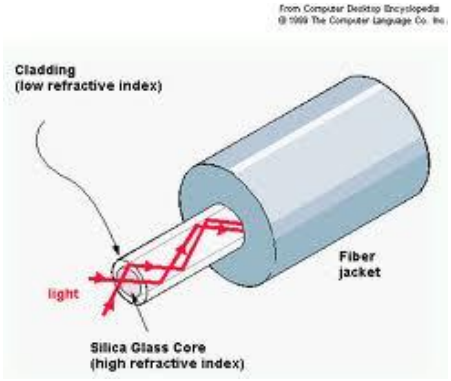
chromatic (compound lens, mirror),
spherical (reduce aperture, plano-convex),
coma (align, reduce aperture),
astigmatism (reduce off-axis mirror, parabolic)

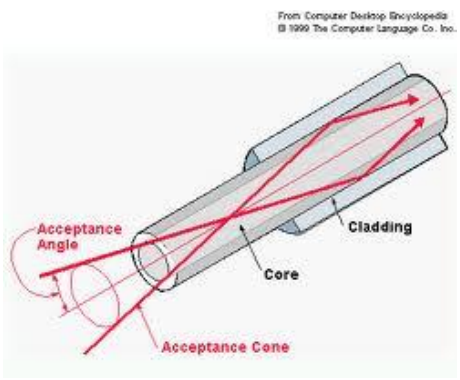
B. Special

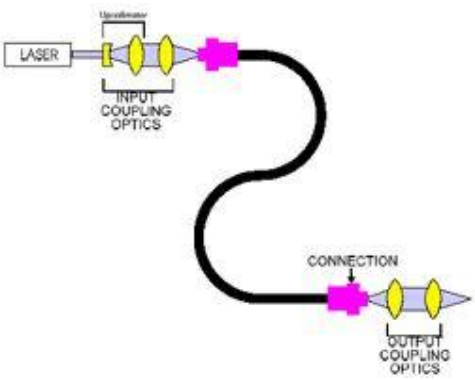
1. Fiber optics — total internal reflection — limits acceptance angle



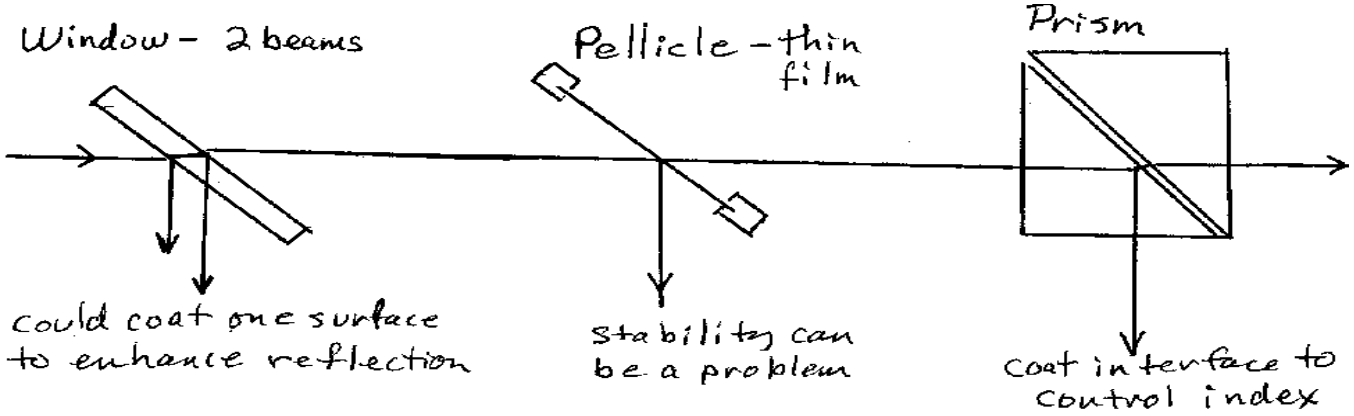
Important to have difference in index, create internal reflection without much loss
Keep angle large by having thin fiber – corollary, harder to insert light beam (bundle)

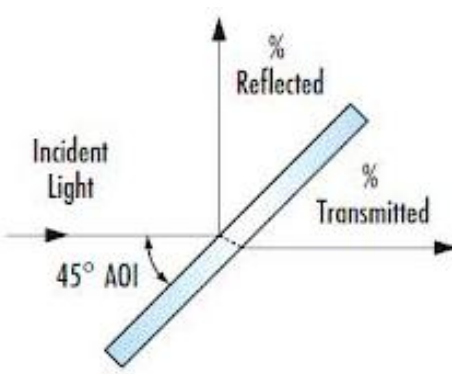


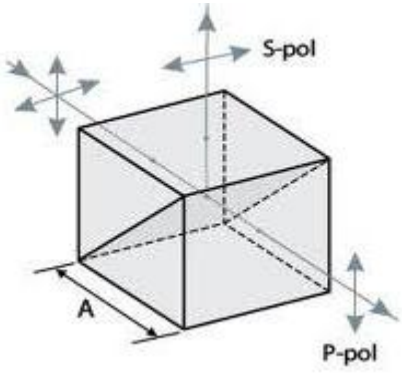


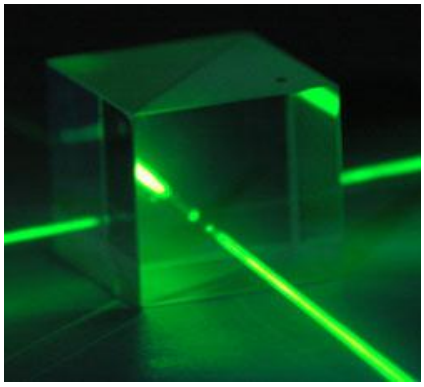


2. Beam Splitter — divides beam in space (can be coating or just surface, can use angle to enhance, single surface best)

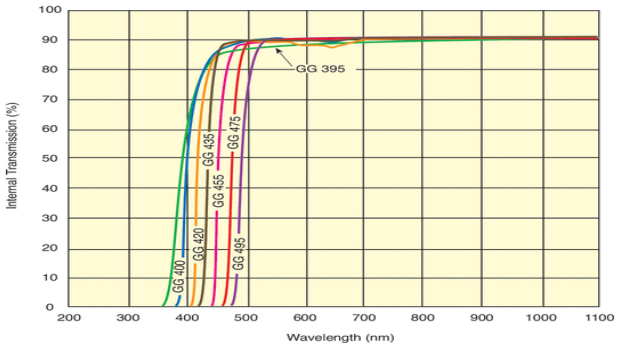


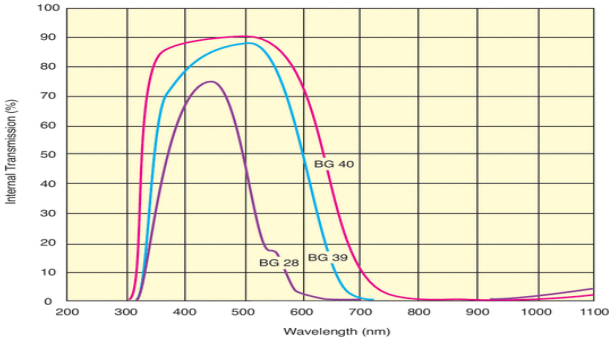


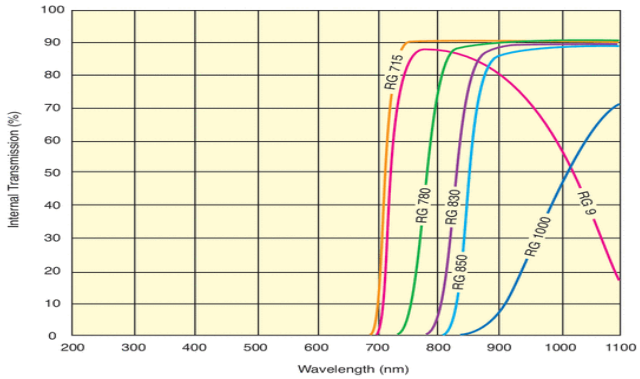


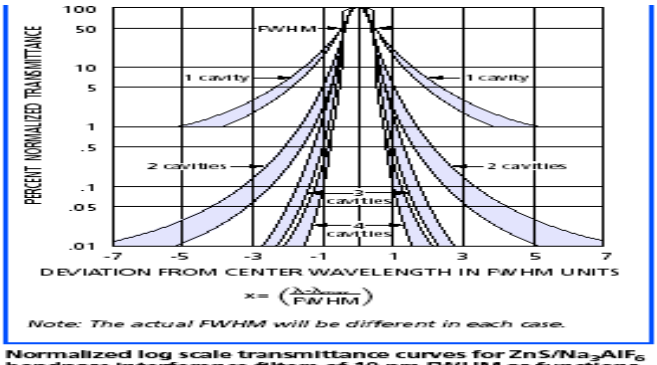


3. ***Filters*** — color filters are glasses with absorbing materials mixed in, ex. transition metal salts, designed as band pass or cut off, progressing out to even IR, also polymer films with dyes







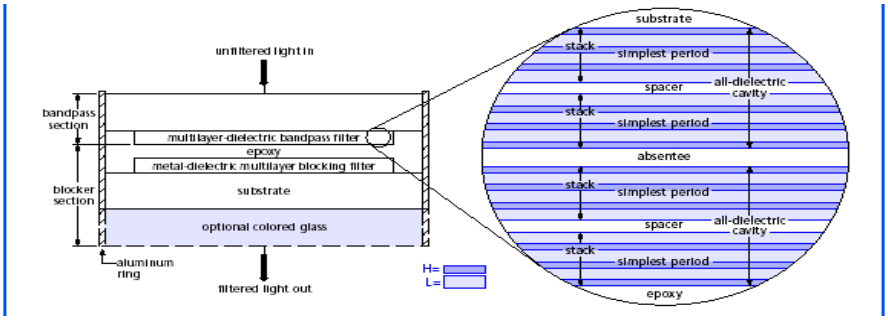


Normalized log scale transmittance curves for ZnS/Na_3AlF_6 bandpass interference filters of 10 nm FWHM as functions of the number of cavities used in filter construction

--*interference* —narrow -band or cut off available: - constructive interference transmit max:

$2d(n^2 - \sin^2\theta)^{1/2} = m/\lambda$ where θ is angle of incidence, m is order, d is spacing, n index, so can select λ_{max} or angle or spacing depending on material.

create with multiple layers of dielectric acting as Fabry-Perot interferometer,



Microscopes imaging and microsampling have huge impact on modern analytical chem

Simplest would be a magnifying lens, basic idea is to collect light from an object with a fast lens and make an image of it that is bigger.

If view by eye, second (set) lens forms eyepiece tp aid in focusing on virtual image at diaphragm

Objective, is the lens or set of lenses that collects light form the object (or specimen)

Characterized by *magnification (10X, 50X etc.)* and *numerical aperture*: **NA = n sin α**

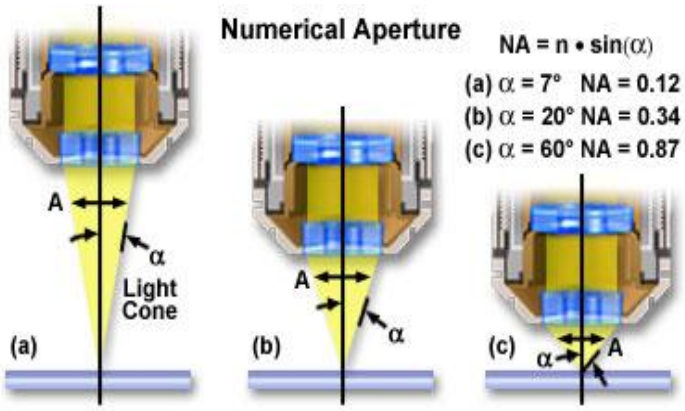


Figure 1

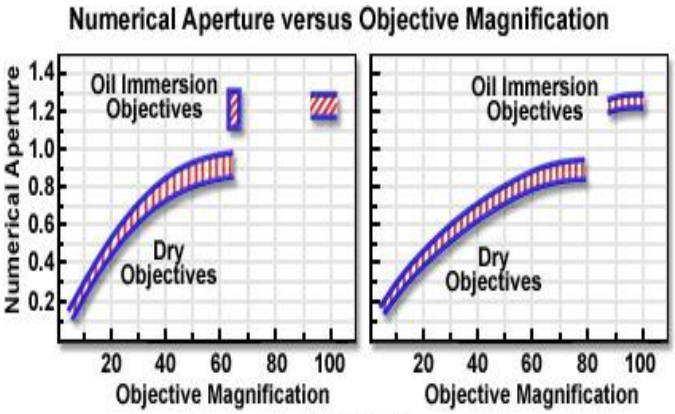


Figure 2

Figure 1

magnification ($m = S_2/S_1$) increase with NA, changing index or add correction can increase NA,

If were simple lens: S_1 would be distance of specimen to objective, effectively the focal length, S_2 "tube length – design length to focus an image at diaphragm,

This is how Olympus defines it, but objective is compound lens, so S_1 seems harder to define, since working distances typically much shorter

Total magnification is product of objective and eyepiece magnifications
Useful range is (500-1000)xNA

Magni-fication	NA	d (μm)		Corrected Magnification	NA	Typical working distance (mm)	
4x	0.10	2.75		10x	0.45	4.0	
10x	0.20	1.10		20x	0.75	0.35	
20x	0.45	0.69		40x (oil)	1.30	0.20	
40x	0.65	0.42		60x (oil)	1.40	0.21	

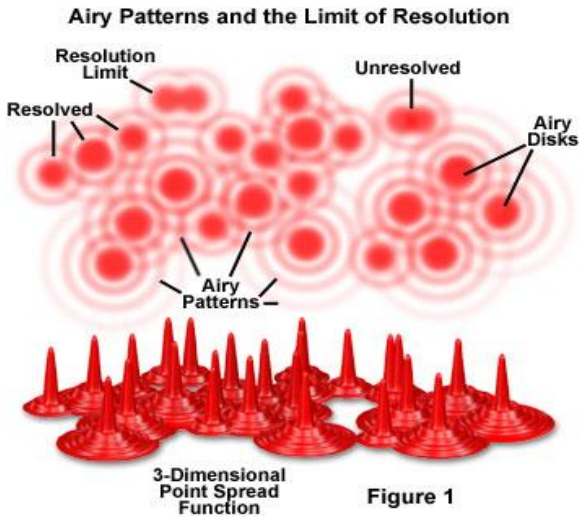


Figure 1

Resolution one can get in an image, minimum distance between objects, ideal → **d = λ/2 NA**
Objects create diffraction patterns, Airy disk, overlap - shorter λ, higher NA more resolved

NA scale sort of backwards of f/# → NA bigger means more light collected

if θ or α is half angle of collection cone, then
NA = n sin θ where n is index of medium, for air ~1
But if use oil immersion, then n~1.5,→ higher NA
Relation to f/# = f/D for lens →

NA = n sin θ = n sin [arctan (D/2f)] ~nD/2f ~ (n/2)[f/#]

Real microscopes are complex, with multiple lenses, some correct for aberrations,
and some act to carry the image to detectors, eye, camera, spectrometer etc.

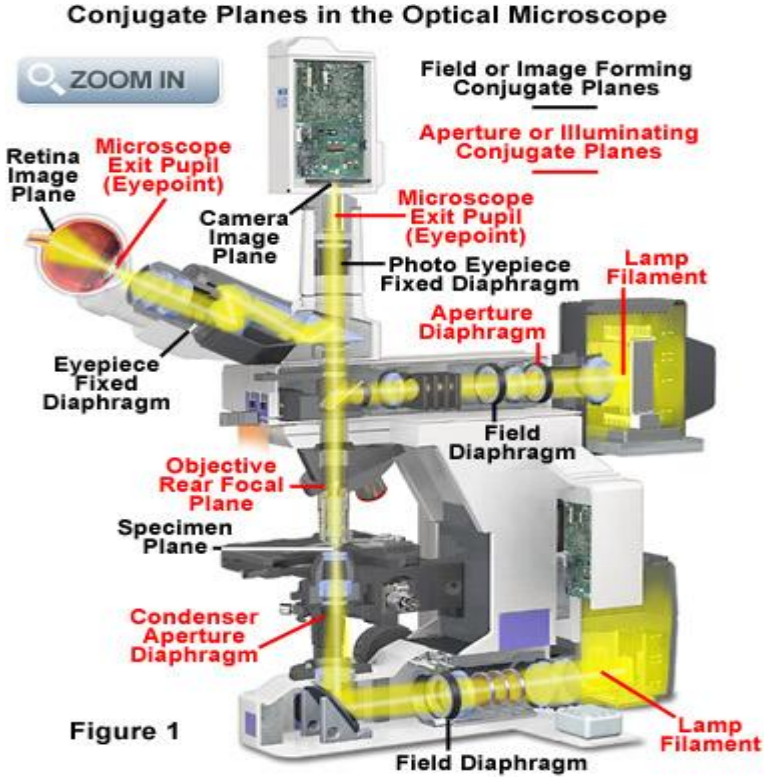


Figure 1

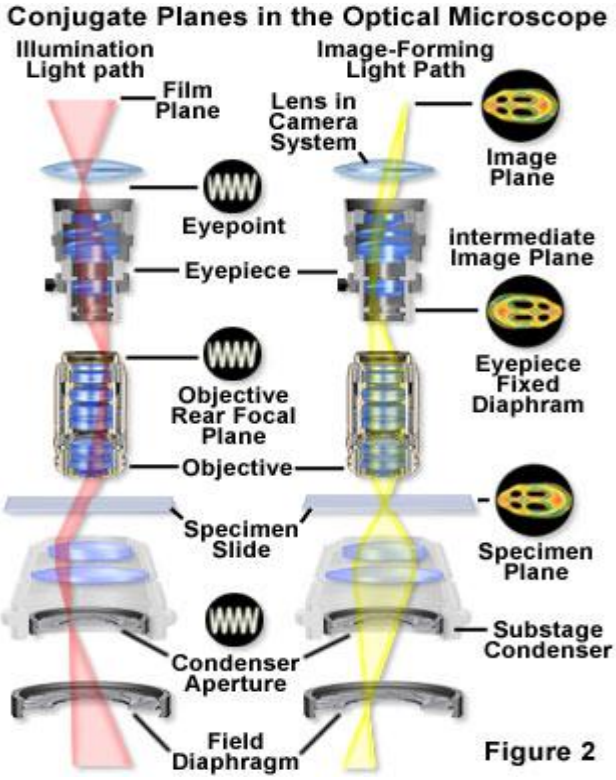


Figure 2

Conjugate planes - about illumination and detection and different planes in which each is in focus

At high magnification, the lens gets very close to the object (specimen) and the properties of the
Sample and slide/coverslip can affect resolution in practice due to aberrations
Traditional objectives focused at 160 mm, so at 40x they would be ~4 mm from the sample
New ones are designed for infinity imaging, create parallel light, make more room for add-on
so an eyepiece refocuses the image, and can add magnification.

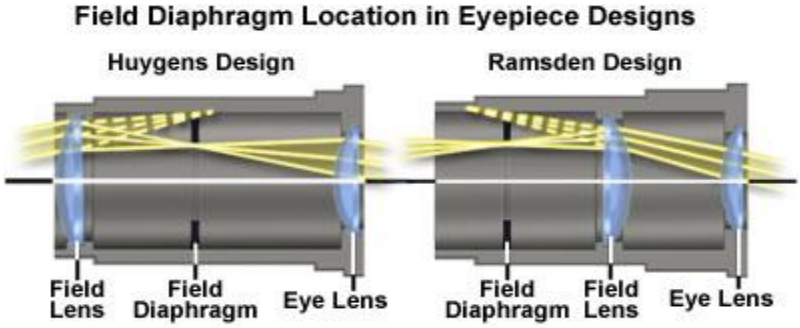


Figure 1

Field of view is controlled by the eyepiece and an intermediate field lens,
Field = fn/m - m = magnification
fn – diameter of view field in image plane,
field size determined by diameter of diaphragm

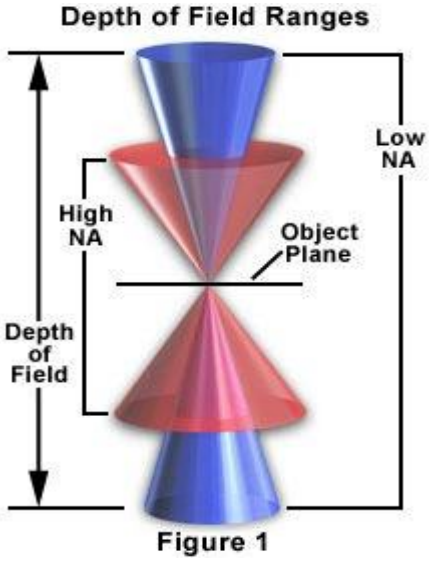


Figure 1

Depth of focus (or field) – d.f. controlled by the NA

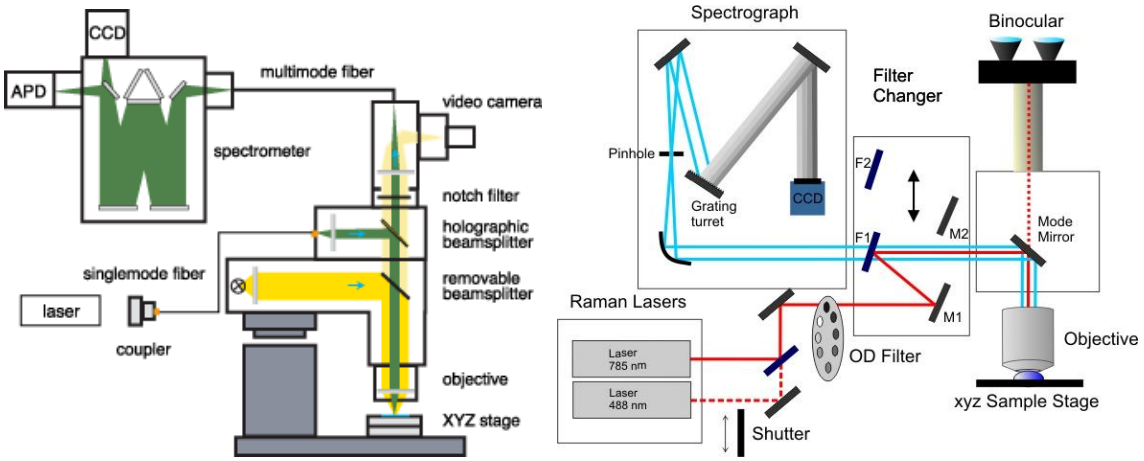
So can see *above and below* the specimen plane, tells what parts above and below in focus. If image on a camera or the like, will be seeing effectively one plane, but if doing spectroscopy can get data from some range through sample
Image is magnified, so has different depth but related

Ex: Magn.	NA	d.f.(μ)	image(mm)
4x	**0.10**	**55.5**	**0.13**
10x	**0.25**	**8.5**	**0.80**
20x	**0.40**	**5.8**	**3.8**

Illumination – since you need light to see an image, much effort has been in illuminator design, idea is not to focus source on specimen but on the aperture of the objective, to create even illumination and no image of the filament, etc.

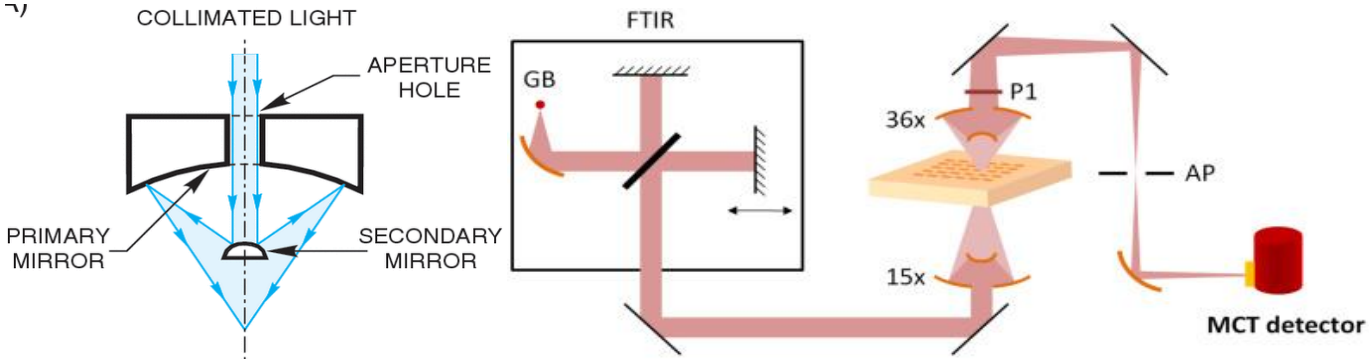
Spectroscopy - the sample is the source, if fluorescence or Raman, which should be evenly excited—or use laser focus to pick out a specific part of sample for spectral analyses—improve resolution over microscope itself. These ideas also useful for absorbance (vis or IR)

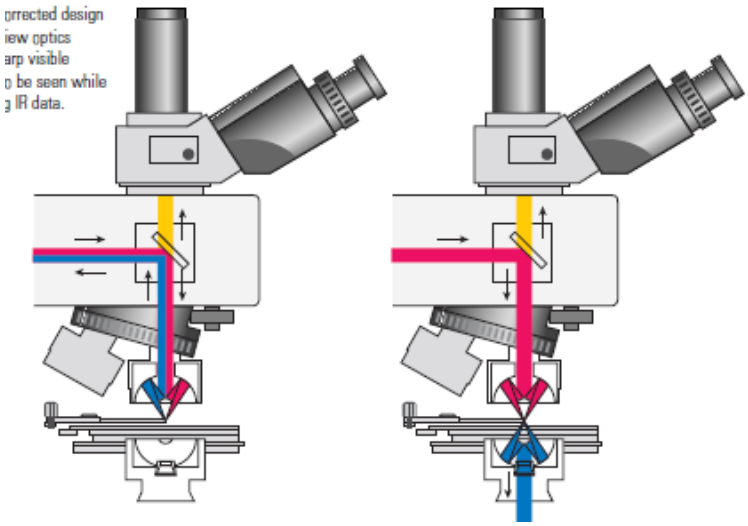
Raman or fluorescence Microscopes

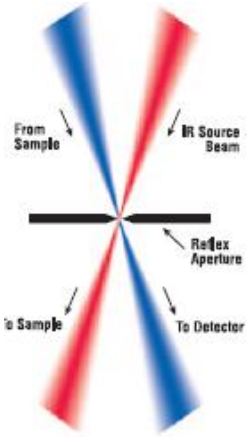


Excitation is often a laser, but now often use non-linear responses to get selectiveity and to get enehanced resolution effects as well. Short wavelengths allow resolutions to ~500 nm, bot bio systems can image parts of cells and thus get information about distribution of species in cell. Using labels in fluorescence can follow bio processes, but they need ot be incorporated. Raman is in principle “label free” but often needs substantial sample size, unless tricks are used like SERS.

IR microscopes—problem of absorption of the lenses, so typically use a mirror optic for objective — Cassegrain collector or use ATR (internal reflection)

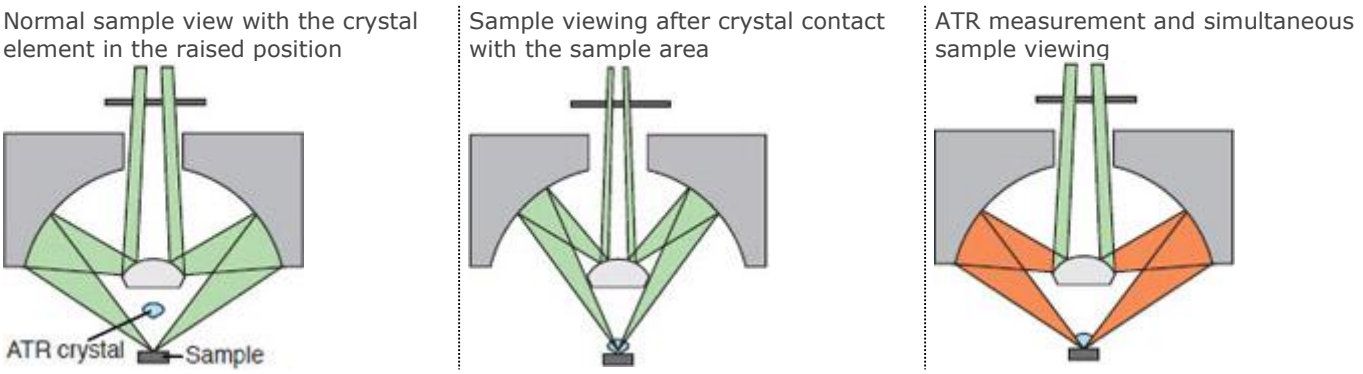






Reflection mode Transmission mode Aperture select part of sample

Big application has become imaging, not just spectroscopy of spot but spatially selective spectra of image, in effect this becomes *chemically edited*. So for materials can see inhomogeneities and identify what they are, for pharma can monitor distributions in formulations of drugs (e.g. tablets, etc), for bio samples can analyze variations in tissue, disease identifications and other biomedical applications. Longer wavelength limits resolution, typically ~5-10 micron.



JASCO ATR objective design

Homework, *will be part of set #2*

—read Chap 3-1, 4, 5 (then 3-2, 3, which carry over to Section 5, Special Optics)

-- to discuss: Problem 3-2, 11, 19,

Problems to do: Ch 3: # 2, 7, 10, 11, 13, and

a. I have a spectrometer that I wish to illuminate. To get the maximum efficiency, I need to image the source on the entrance slit (100 μ x 5 mm). Only the amount of power incident on the opening of the slit makes it to the detector. To properly use the spectrometer, the incident light should enter with an F/4 cone. You have a quartz halogen lamp (with a filament 1 mm x 10 mm) and three lenses, each 50 mm in diameter, with focal lengths of 50, 200 and 1000 mm. What lens do you chose and where do you place it and the source to get the best throughput efficiency at the slit?. Why?
b. I want to build a sample chamber for microsampling (e.g. ~0.1-1.0 mm diam.) using an FTIR spectrometer, to collect spectra in the 3-10 micron range. Should I use lenses or mirrors to focus the output of the interferometer on the sample and collect the light again and refocus on the detector (area 1 mm^2)? Why? What kind (size, focal length, material/coating) lenses or mirrors would be needed to create an essentially straight design (i.e. compact) that will match both focusing requirements.

Links to optics etc:

Iowa State course, properties of light (sort of just formulas),
http://avogadro.chem.iastate.edu/CHEM513/513-1.pdf
physicaloptics
http://avogadro.chem.iastate.edu/CHEM513/513-2.pdf
http://avogadro.chem.iastate.edu/CHEM513/513-3.pdf

Optics companies: (first two, more precision items)

Newport (some tutorial info is contained on specific product pages, like ashpheric lenses, etc.)

http://www.newport.com/Optics/5677806/1033/section.aspx

Melles-Griot

www.cvimellesgriot.com/Products/Optical-Components.aspx

Edmund Optics
http://www.edmundoptics.com/onlinecatalog/browse.cfm

Edmund Scientific, wide variety of lenses and mirrors, originally for astronomy hobbyist
http://scientificsonline.com/category.asp_Q_c_E_424411

American Science Surplus Center—great source for cheap optics
http://www.sciplus.com/category.cfm?subsection=21

Mark Optics, CA
http://markoptics.com/pages/products.htm

Microscopes:

Nikon and Olympus both have excellent tutorials on microscopy
http://www.microscopyu.com/articles/formulas/
http://www.olympusmicro.com/index.html