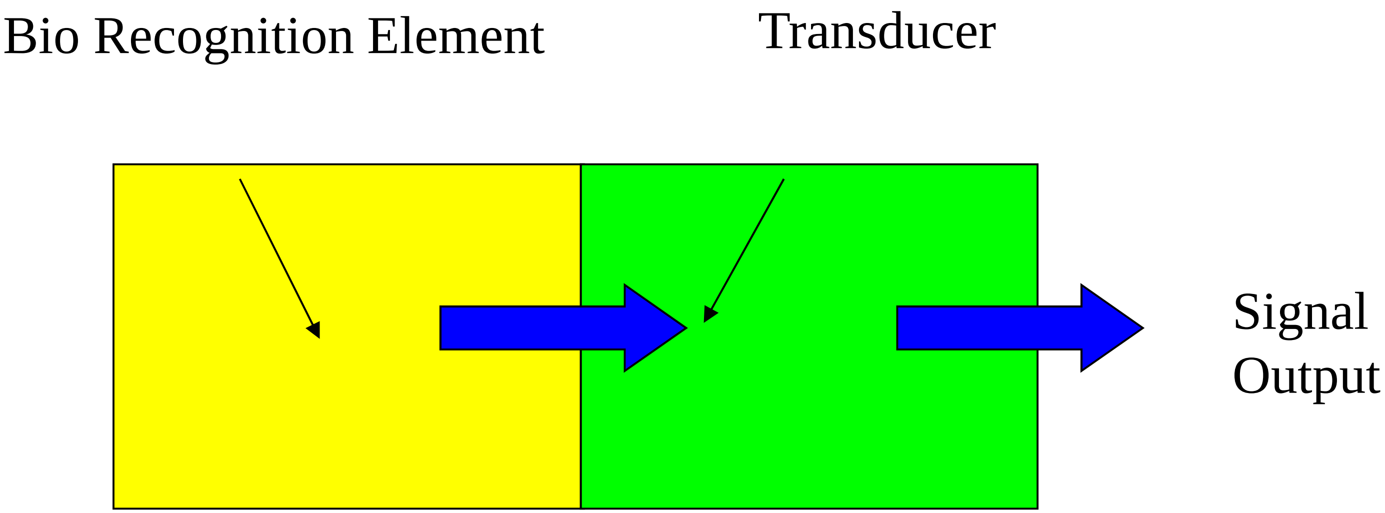
Surface Plasmon Resonance

Prof. Xingwei Wang

Biosensor



Requires:
Sample
Immobilization

Enzymes;
Antibodies;
Receptors;
Whole
cells...

Electrochemical

Optical

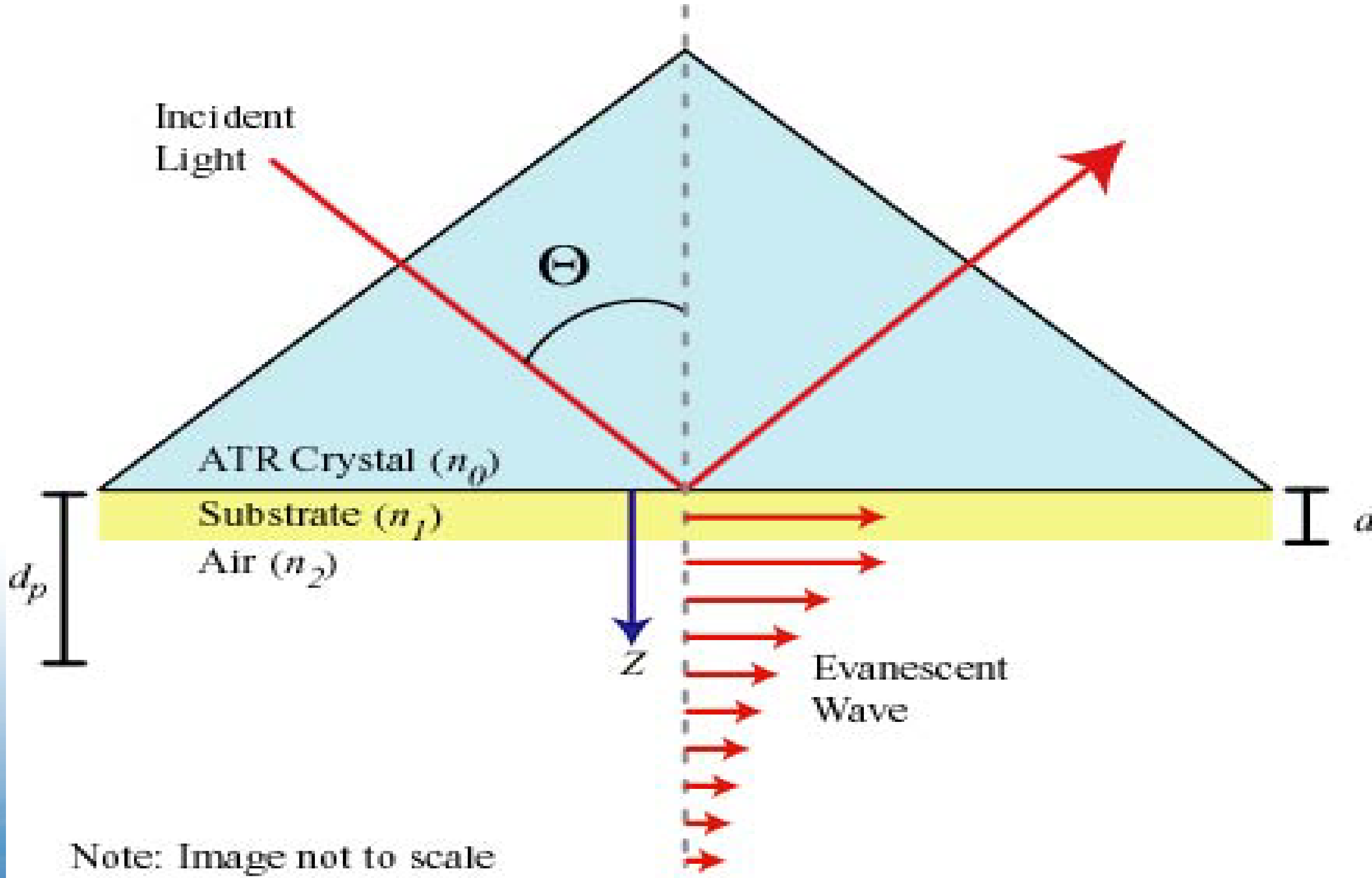
Requires:

Simple read out and data interpretation;

Easy to use;

Quick response.

Evanescent Wave



Evanescent wave

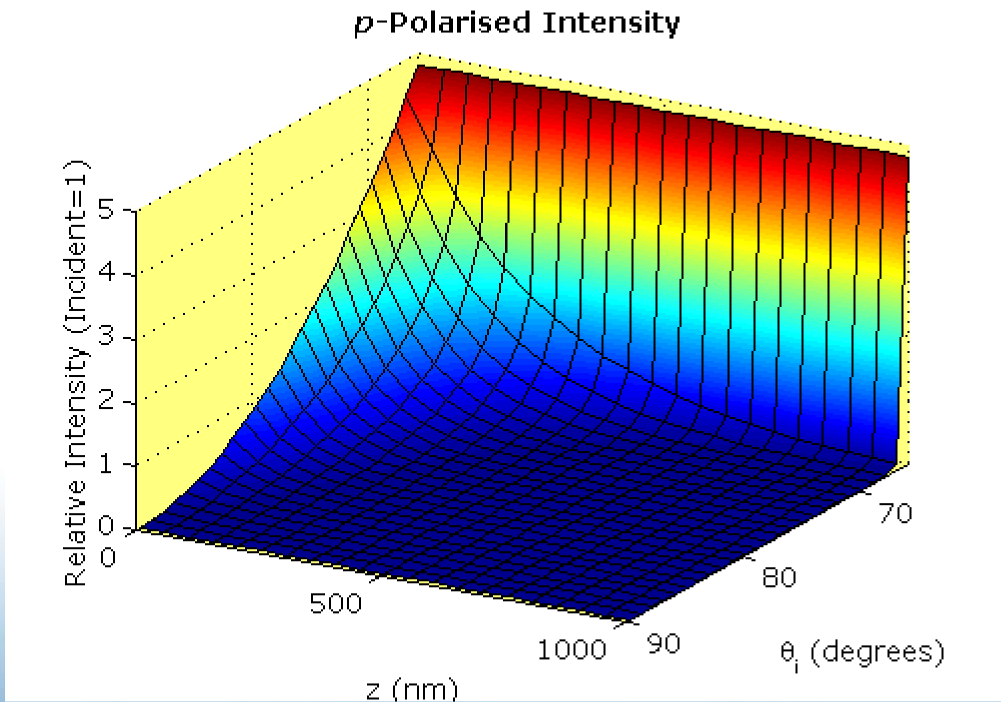
- Evanescent wave: a few hundred nanometers
- Decays exponentially over a fraction of the wavelength
- Evanescent wave and the resonance angle depend on the refractive index at the interface.

Penetration depth

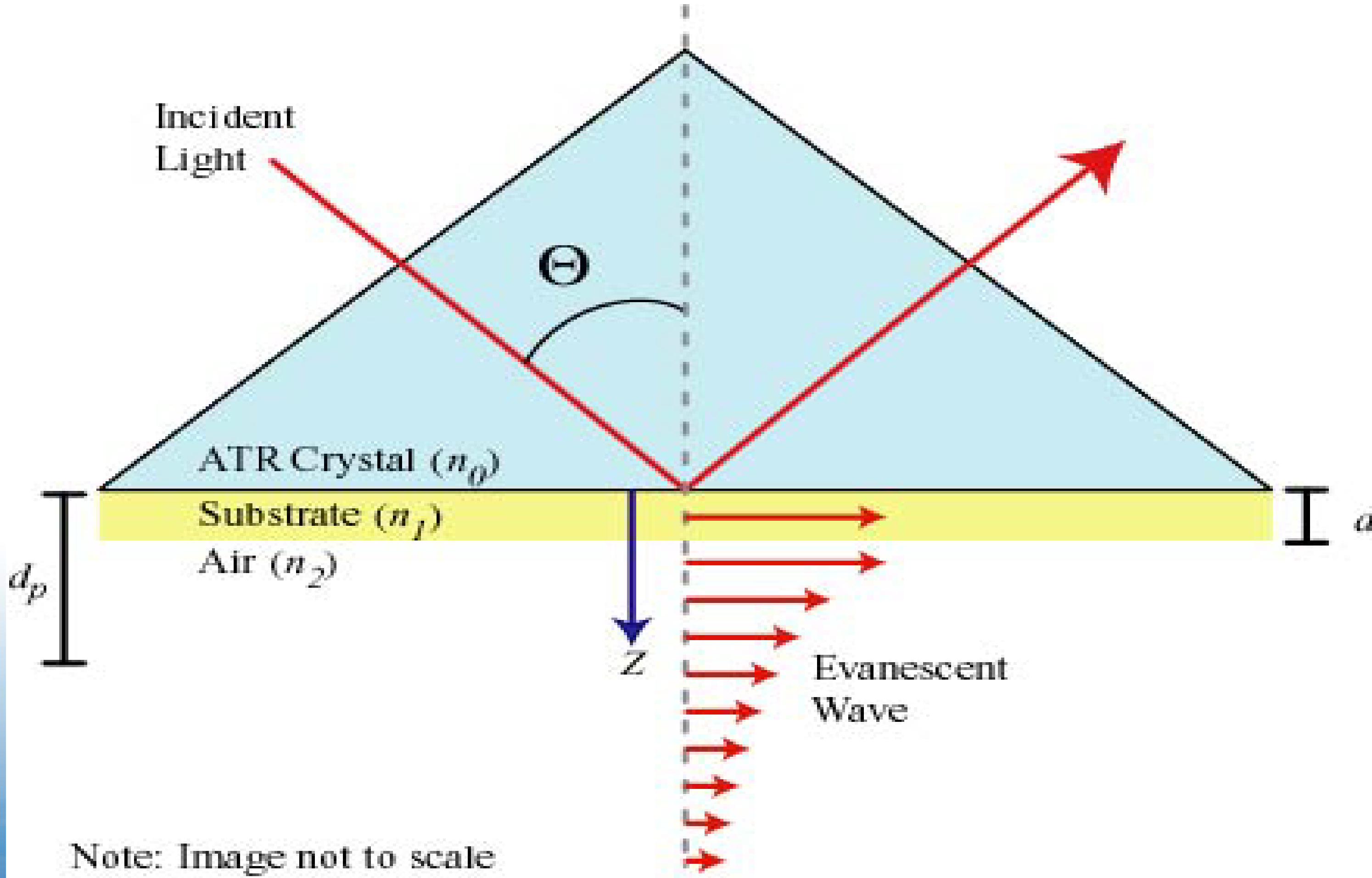
$$d_p = \frac{\lambda}{2\pi({n_{co}}^2 \sin^2\theta_1 - {n_{cl}}^2)^{1/2}}$$

- where θ1 is the internal incident ray angle with the normal to the core/cladding interface
- Penetration depth provides a spatial separation between the fluorescent complexes bound to the core and those free in solution
- Highly specific antibody binding event
- Eliminates the need for the washing step

Intensity for 532 nm light at a quartz-water interface



Evanescent Wave



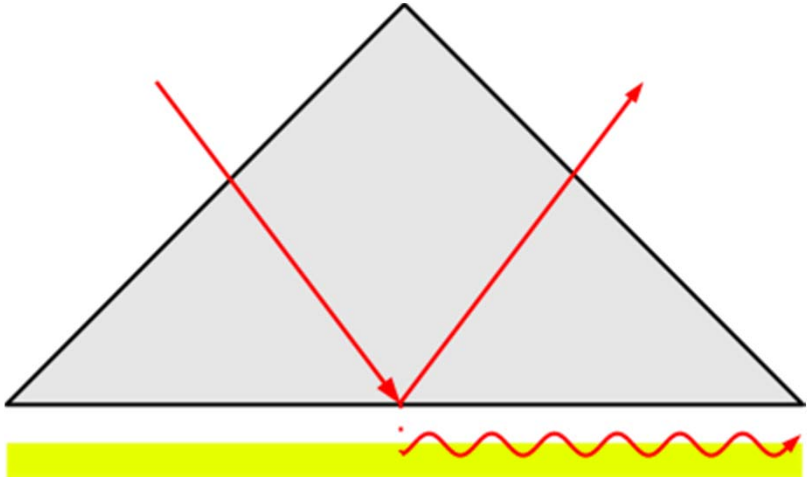
Surface Plasmon Resonance

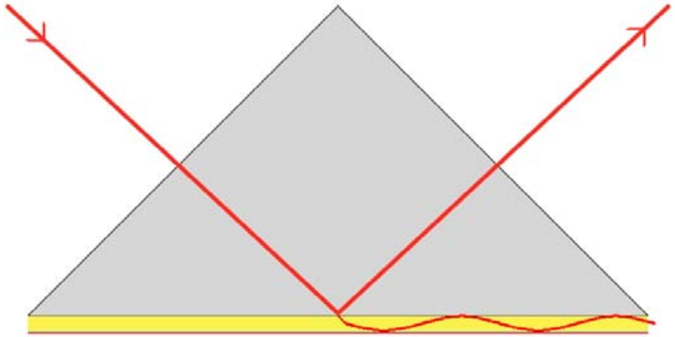
- Interface: high refractive index; thin layer with good electric conductivity; a medium of low refractive index
- Evanescent wave interacts with free electrons in the conductive layer
- Give rise to “plasmons”
- Energy is lost from the reflected light
- Results in a minimum of the reflected intensity at the resonance angle.

Surface plasmons

- Surface electromagnetic waves
- Propagate parallel along a metal/dielectric interface
- Very sensitive to any changes of this boundary

Two configurations





Otto setup, the light is shone on the wall of a glass block, typically a prism, and totally reflected. A thin metal (for example gold) film is positioned close enough, that the evanescent waves can interact with the plasma waves on the surface and excite the plasmons.

• Typical metals: silver and gold.

Kretschmann configuration, the metal film is evaporated onto the glass block. The light is again illuminating from the glass, and an evanescent wave penetrates through the metal film. The plasmons are excited at the outer side of the film. This configuration is used in most practical applications.

Biosensing

- Measure refractive index changes due to the absorption of material to the sensor surface
- Refractive index changes are proportional to the mass of the molecules that enter the interfacial layer

Biosensing

- Metal/dielectric interface
- Truly reagentless sensor (label-free)
- Antibody is immobilized on the surface of the metal at which the surface wave is generated.
- On binding a large analyte the refractive index within the region of the surface plasmon evanescent field changes
- Matching requirements for surface plasmon generation are correspondingly altered
- Change in the angle of the incident light required to achieve resonance

UMASS University of Massachusetts Lowell

Commercial instrument

- BIAcore from Pharmacia Biosensor AB in 1990
- Autosampler
- Integrated fluid-handling system
- High-resolution sensor on top of a microflow chamber
- Temperature-stabilized environment
- Become a standard technique in many biological and medical research areas.

Schematic of SPR setup

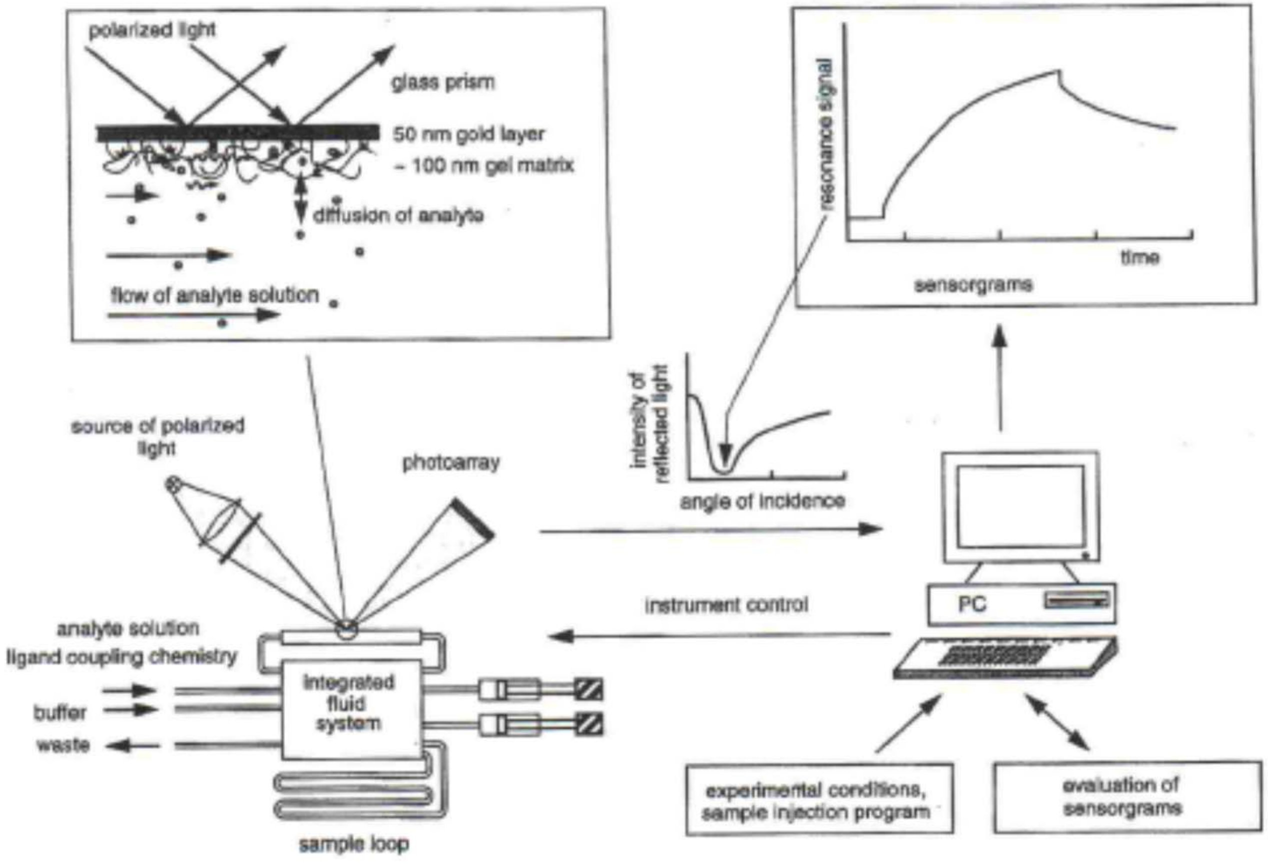


Figure 11.1. Basic scheme of surface plasmon resonance measurements in a BIAcore

University of Massachusetts UMASS Lowell

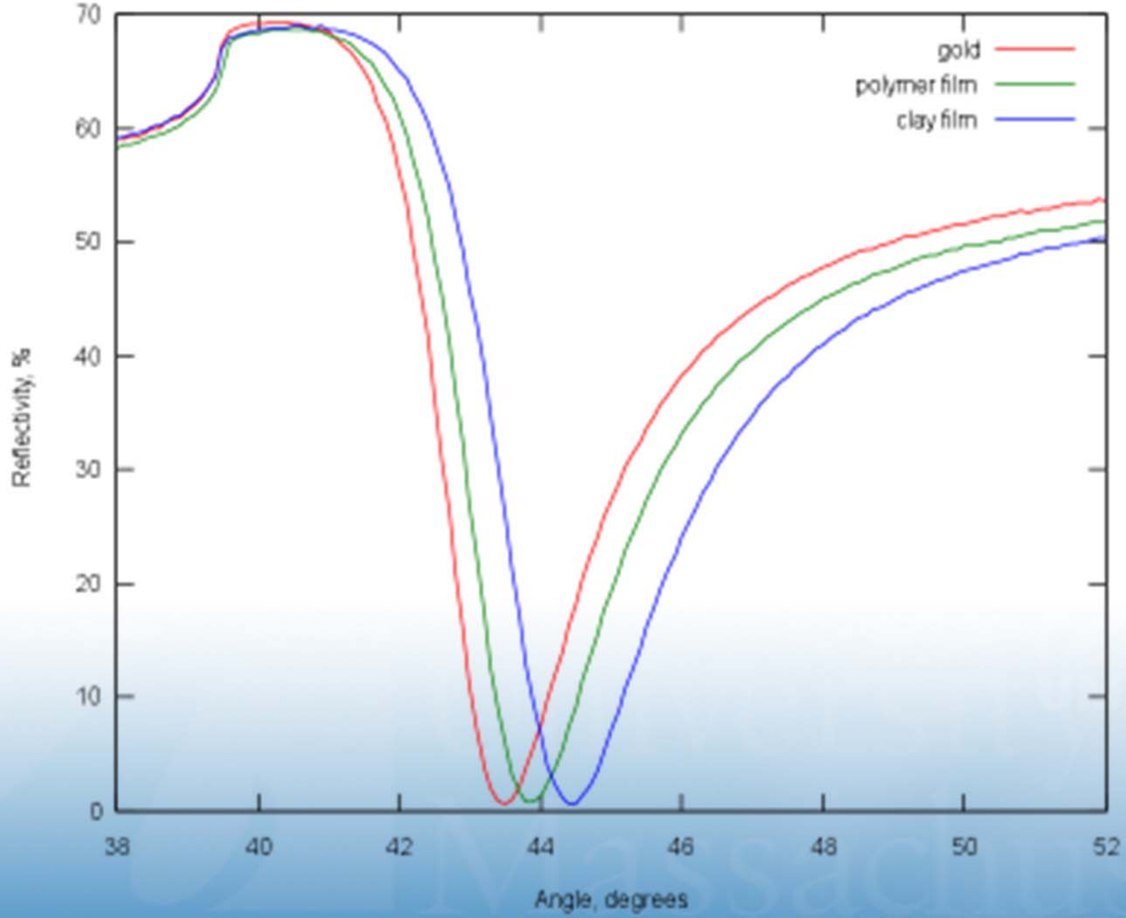
Another commercial instrument

- IBIS; Intersens, Amersfoort, Netherlands
- Only a few users
- Fiber-optic -> remote sensing
- Light intensity is measured as a function of wavelength instead of angle of incidence

Applications

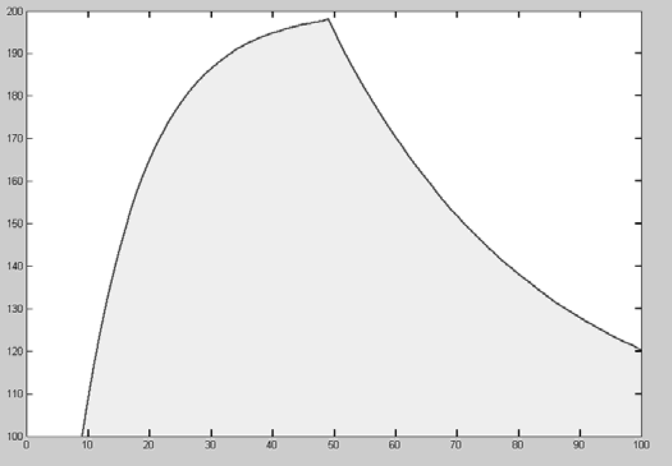
- Linear relationship between resonance energy and mass concentration
- Analyte and ligand association and dissociation ; rate constants; equillibrium constants can be calculated.

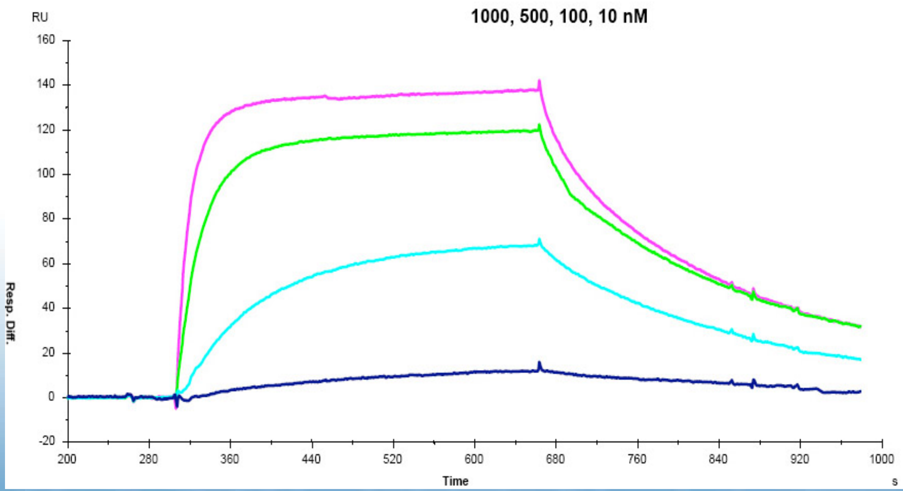
Examples: measurement of film thickness



Example: Binding constant determination

- Binding constant -> affinity of two ligands
- Association rate divided by the dissociation rate
- Prey ligand; bait layer; a solution without the prey -> microflow system





Association and dissociation signal

Output from Biacore

University of Massachusetts UMASS Lowell

Video

- http://www.youtube.com/watch?v=sM-VI3alvAI (principle)

video

- http://www.youtube.com/watch?v=z9Rro7FDeDo (SPR principle)

- http://www.youtube.com/watch?v=EpGx-SUsfQ0&list=TL3VyJvKZKiws (SPR imaging)

University of Massachusetts UMASS Lowell

Commercially available SPR system video

- http://www.youtube.com/watch?v=o8d46ueAwXI (GE)

- http://www.youtube.com/watch?v=iVHxQ3IJBzM (KMAC system)

Video

- http://www.youtube.com/watch?v=YAJ1b68mHtY (detect small molecule label-free)

Combined with other sensing methods

- Fluorescence
- Raman scattering
- Surface plasmon resonance imaging (surface is patterned with different biopolymers)
- Michelson Interferometer

Michelson Interferometer

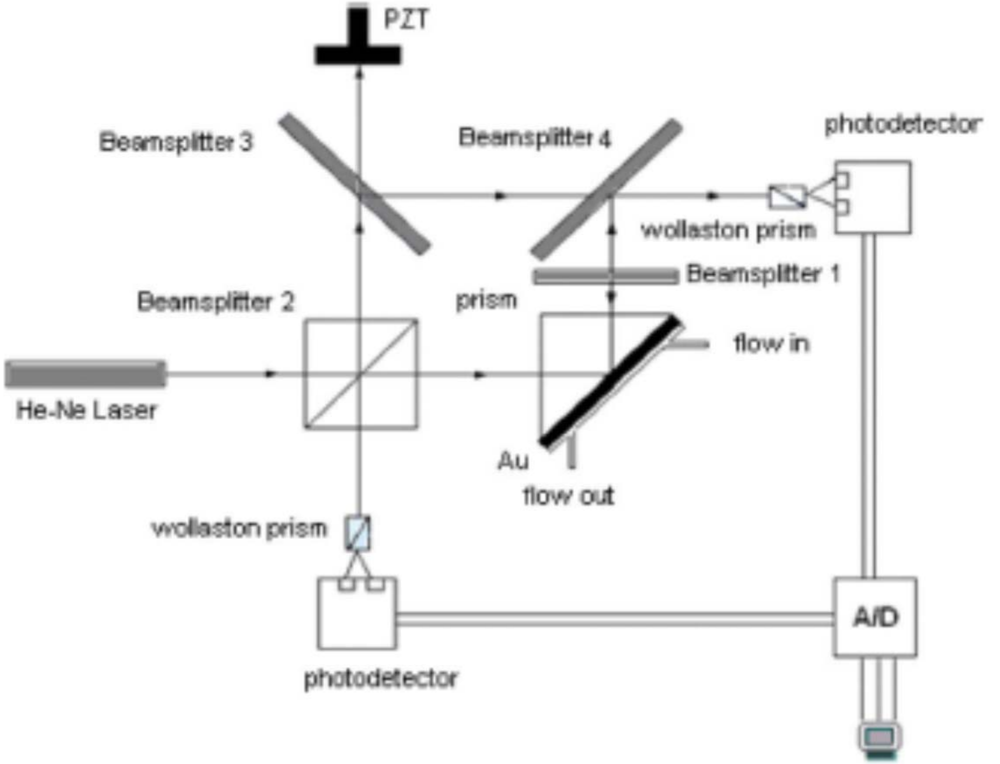


Fig. 1. Experimental setup combining Mach–Zehnder and Michelson interferometer configurations for real-time differential phase measurement and comparison.

Localized surface plasmon resonance (LSPR)

- Nanometer-sized metallic structures
- Extraordinary optical properties of noble metal nanoparticles
- Nanoscale chemosensors and biosensors
- Nanoparticles of noble metals exhibit strong UV-Vis absorption bands

Advantages

- Ag nanoparticle
- Ultrasensitive biodetection
- Extremely simple
- Small
- Light
- Robust
- Low-cost instrumentation
- Less than one picomolar up to micromolar concentrations
- Medical diagnostics, biomedical research, and environmental science

Principle

- Transducing small changes in refractive index near the noble metal surface into a measurable wavelength shift response

$$\Delta R_{max} = m(n_{adsorbate} - n_{blank})\left[\exp\left(-\frac{2d_{adsorbate}}{l_d}\right)\right]\left[1-\exp\left(-\frac{2d_{adsorbate}}{l_d}\right)\right]$$

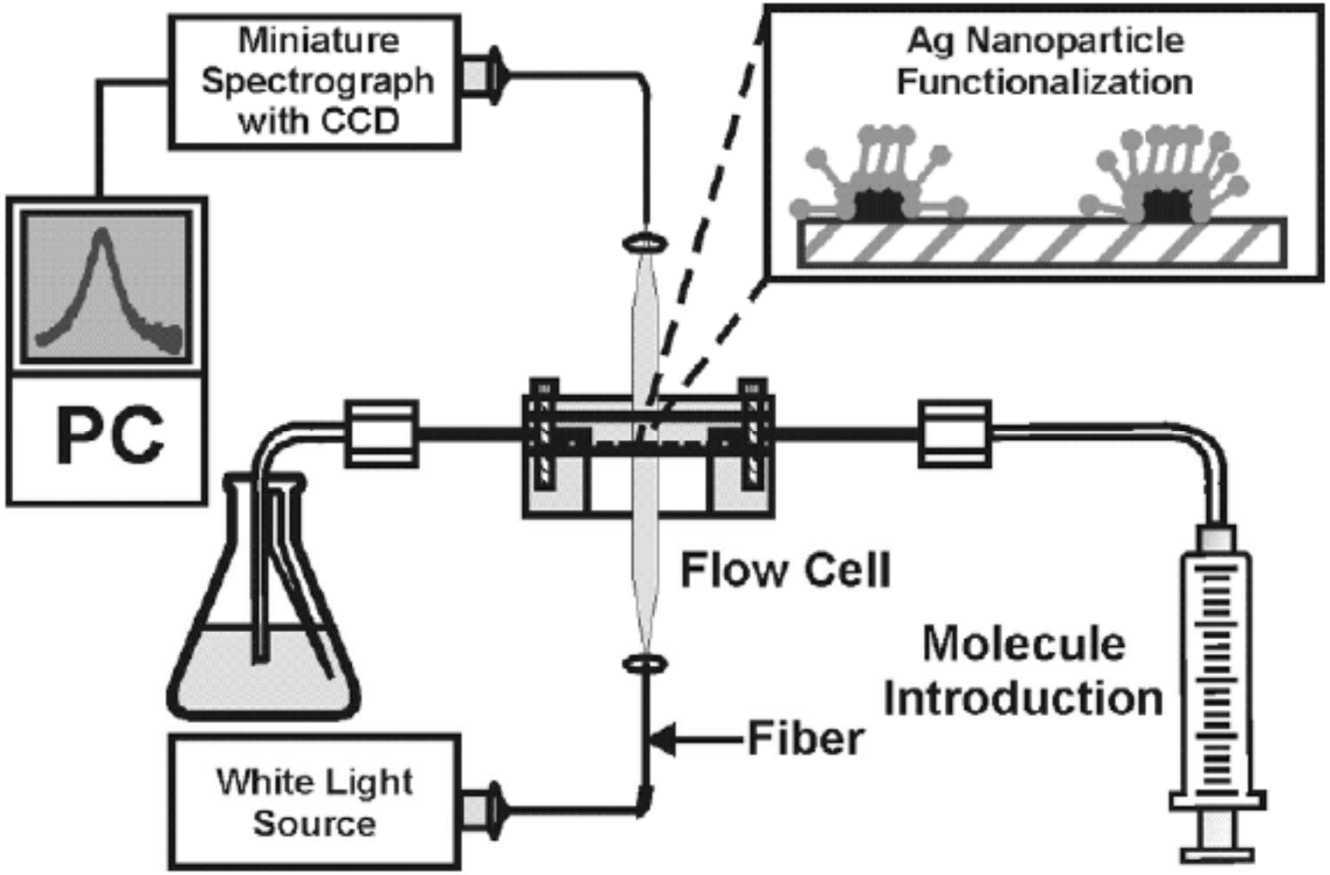
- where m is the refractive index sensitivity of the sensor, $n_{adsorbate}$ and n_{blank} are the refractive indexes of the desired adsorbate and bulk environment prior to the sensing event, respectively, $d_{adsorbate}$ is the effective thickness of the adsorbate layer, and l_d is the characteristic electromagnetic field decay length associated with the sensor.

Comparison

- Flat surface SPR sensors have a large refractive index sensitivity, ~$2x10^6$ nm/RIU
- LSPR nanosensors have a modest refractive index sensitivity, ~$2x10^2$ nm/RIU.
- SPR sensors have a decay length on the order of ~200 nm
- For the nanoparticles and the corresponding LSPR nanosensor, a much shorter electromagnetic field decay length (~6 nm)
- This short decay length gives rise to the large sensitivity of the LSPR nanosensor

University of Massachusetts UMASS Lowell

Instrumental diagram for the LSPR nanosensor experiment



Results

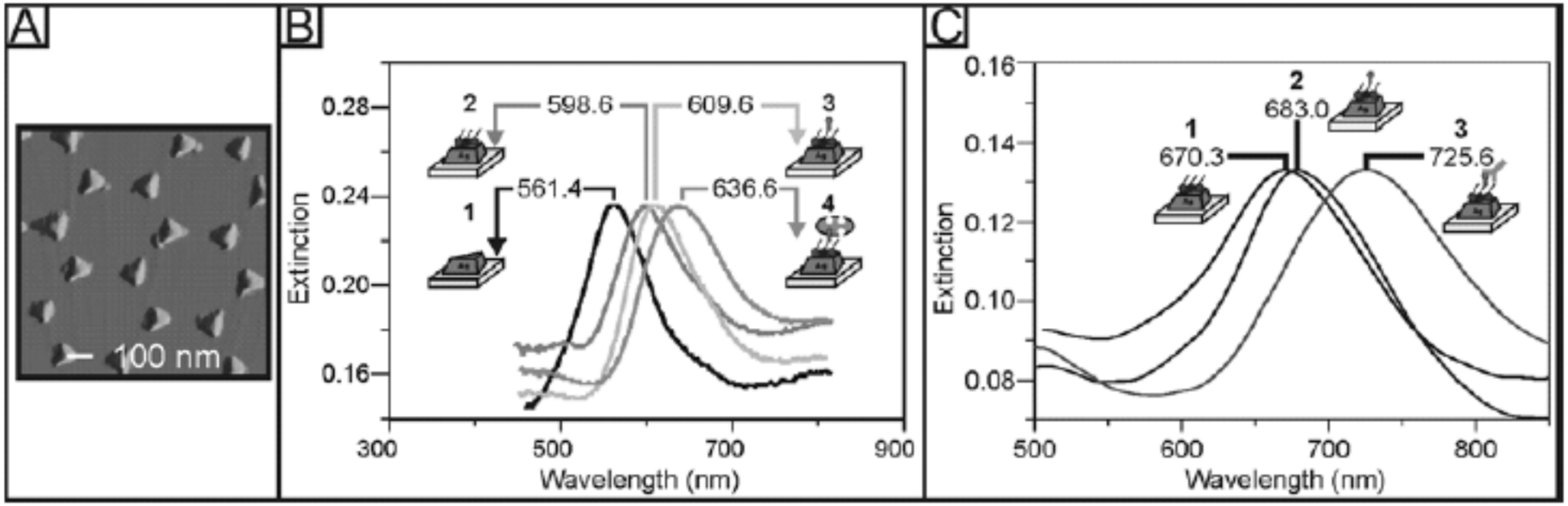
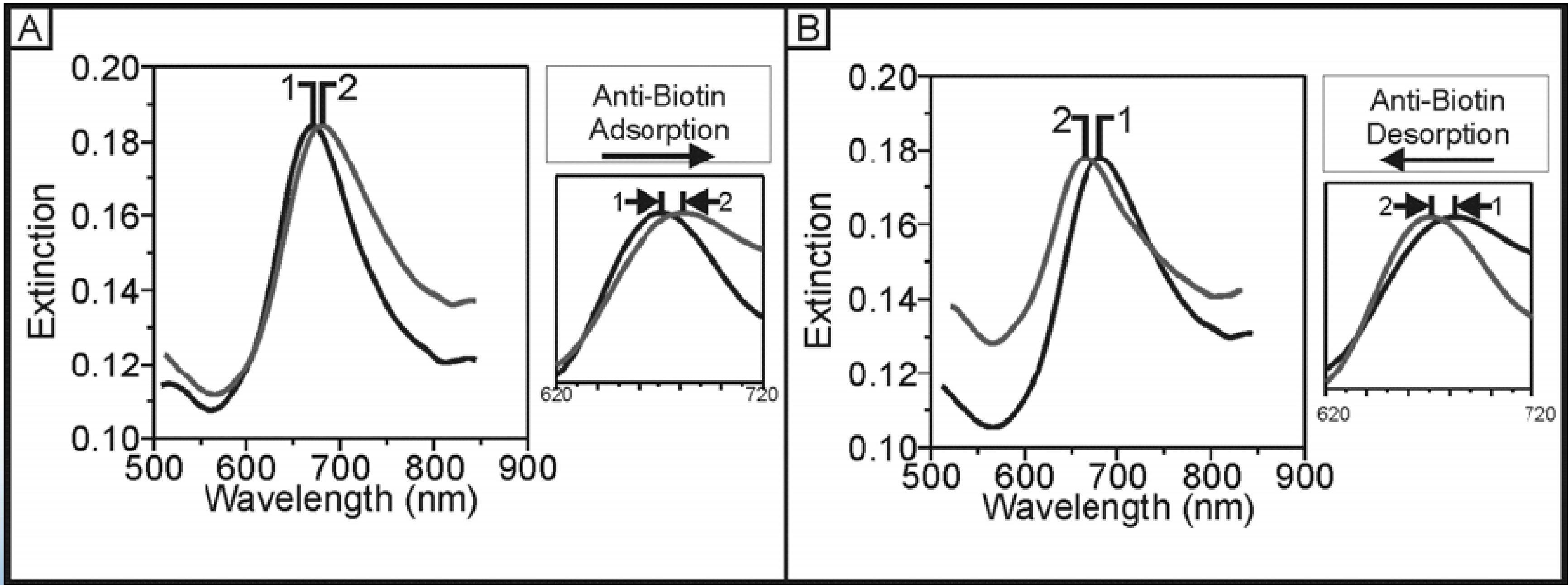


Figure 2. (A) Tapping mode AFM image of Ag nanoparticles. (B) LSPR spectra of each step in the surface modification of NSL-derived Ag nanoparticles to form a biotinylated Ag nanobiosensor and the specific binding of streptavidin. (C) Smoothed LSPR spectra for each step of the preparation of the Ag nanobiosensor, and the specific binding of anti-biotin to biotin.

University of Massachusetts UMASS Lowell

Adsorption/Desorption



Performance

- Time scale for these events appears to be less than a minute
- Binding of DNA and proteins
- Future work: miniaturization of the sensor, linkage of the sensor to drug delivery chips, and biocompatibility

Other applications

- http://www.youtube.com/watch?v=uO2XfnnD57I&list=TL3VyJvKZKiws (SPR for drug development)

Surface plasmon resonance

- **Surface plasmon resonance** (SPR) is the collective oscillation of electrons in a solid or liquid stimulated by incident light.
- The resonance condition is established when the frequency of light photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei.

Plasmon

- Plasmons are collective oscillations of the free electron gas density, for example, at optical frequencies.
- Since plasmons are the quantization of classical plasma oscillations, most of their properties can be derived directly from Maxwell's equations.

Plasmons

- An oscillation of free electron density with respect to the fixed positive ions in a metal.

Plasmon

- imagine a cube of metal placed in an external electric field pointing to the right.
  - Electrons will move to the left side (uncovering positive ions on the right side) until they cancel the field inside the metal.
  - If the electric field is removed, the electrons move to the right, repelled by each other and attracted to the positive ions left bare on the right side.
  - They oscillate back and forth at the plasma frequency until the energy is lost in some kind of resistance or damping. Plasmons are a quantization of this kind of oscillation.

Plasmon

- http://www.youtube.com/watch?v=ow9MOZ3Eeqg&list=PLB41E68B9D29A63F8 (plasmon oscillation)

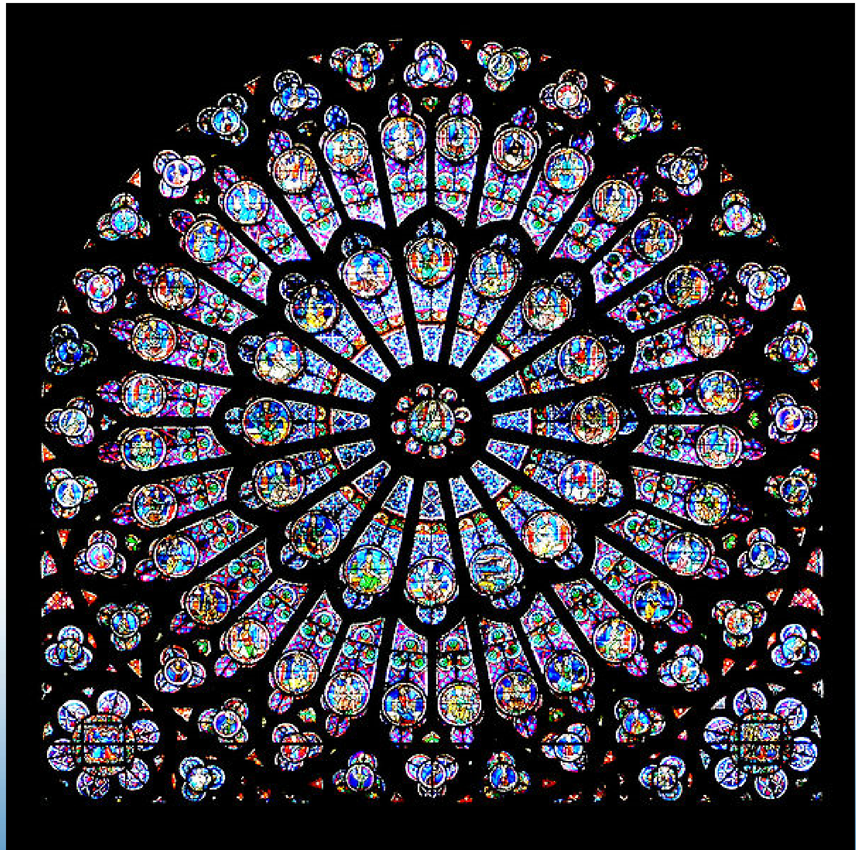
Plasmon

- Plasmons play a large role in the optical properties of metals.
- Light of frequency < the plasma frequency -> reflected
  - because the electrons in the metal screen the electric field of the light.
- Light of frequency > the plasma frequency -> transmitted
  - because the electrons cannot respond fast enough to screen it.

Plasmon

- In most metals, the plasma frequency is in the ultraviolet, making them shiny (reflective) in the visible range.
- Some metals, such as copper and gold, have electronic interband transitions in the visible range, whereby specific light energies (colors) are absorbed, yielding their distinct color.
- In semiconductors, the valence electron plasma frequency is usually in the deep ultraviolet, which is why they too are reflective.

Stained glass



- Gothic stained glass rose window of Notre-Dame de Paris.
- The colors were achieved by colloids of gold nano-particles.
- Gold – red
- Silver - yellow

Surface plasmons control colors of materials

- Controlling the particle's shape and size determines the types of surface plasmons that can couple to it and propagate across it.
- This in turn controls the interaction of light with the surface.

Others

- http://www.youtube.com/watch?v=3J9aUQSK_QE (Photothermal Effect From Local Surface Plasmon Resonance)
- plasmonic photothermal therapy

Others

- http://www.youtube.com/watch?v=bQ6u71T8W-s (Characterizing Plasmons in Nanoparticles and Their Assemblies with Single Particle Spectroscopy)

References

- **Biosensors and their applications**
  Edited by Victor C. Yang and That T. Ngo, 2000, Kluwer Academic/Plenum Publishers, New York, ISBN 0-36-46087-4
- **Highly sensitive surface plasmon resonance optical biosensor based on the use of differential phase Mach-Zehnder interferometer**
  Ho, H.P.; Wu, S.Y.; Law, W.C.; Chinlon Lin;
  Lasers and Electro-Optics, 2004. (CLEO). Conference on
  Volume 2, 16-21 May 2004 Page(s):2 pp. vol.2
- **Surface Plasmon Resonance Biosensor Incorporated in a Michelson Interferometer With Enhanced Sensitivity**
  Yuan, W.; Ho, H. P.; Wong, C. L.; Kong, S. K.; Lin, C.;
  Sensors Journal, IEEE
  Volume 7, Issue 1, Jan. 2007 Page(s):70 - 73

University of Massachusetts UMASS Lowell