TUNTWIN's Workshop

Session A: Introductory session

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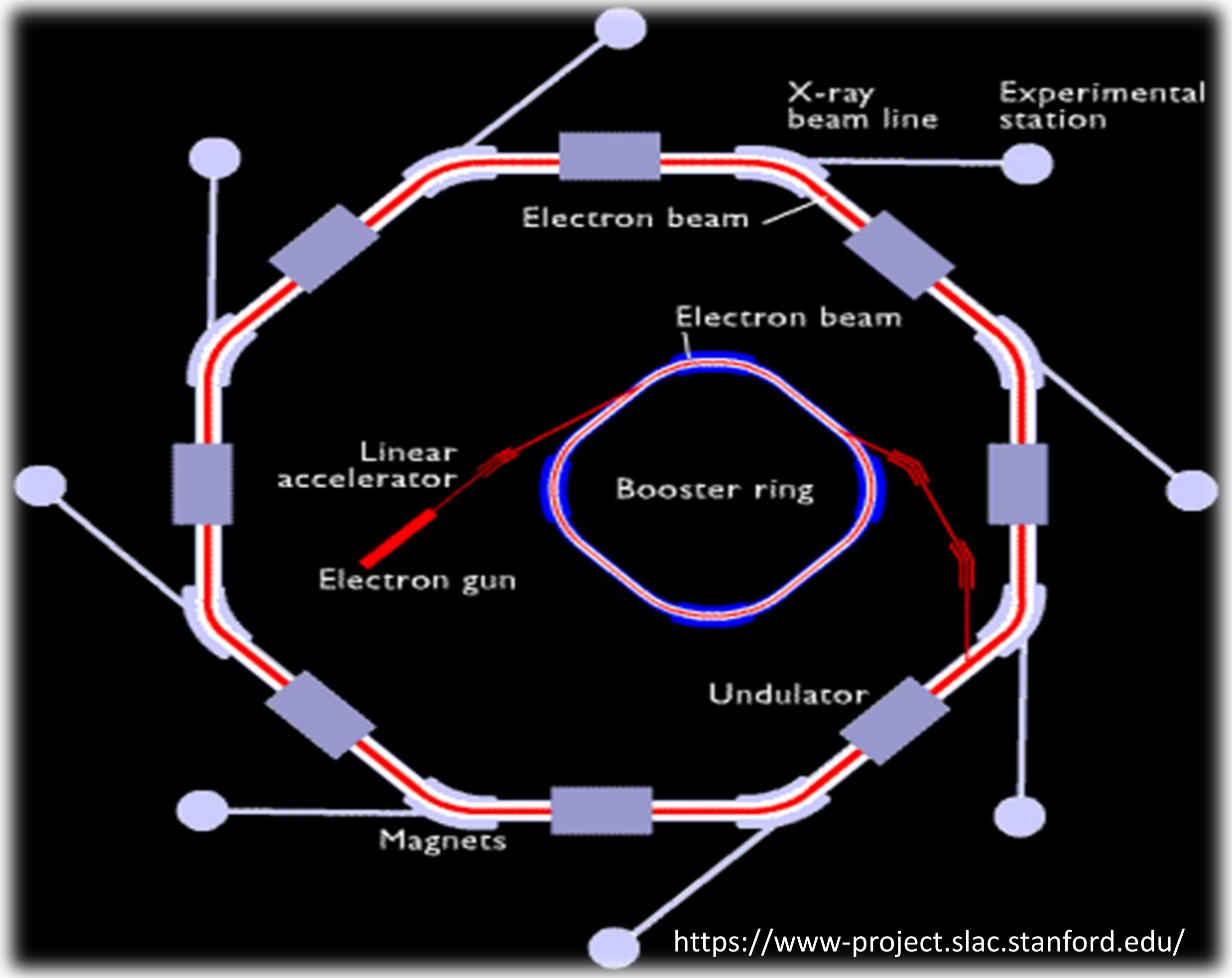
Session A: Introductory session

An overview of the synchrotron radiation techniques: spectroscopy, scattering and imaging

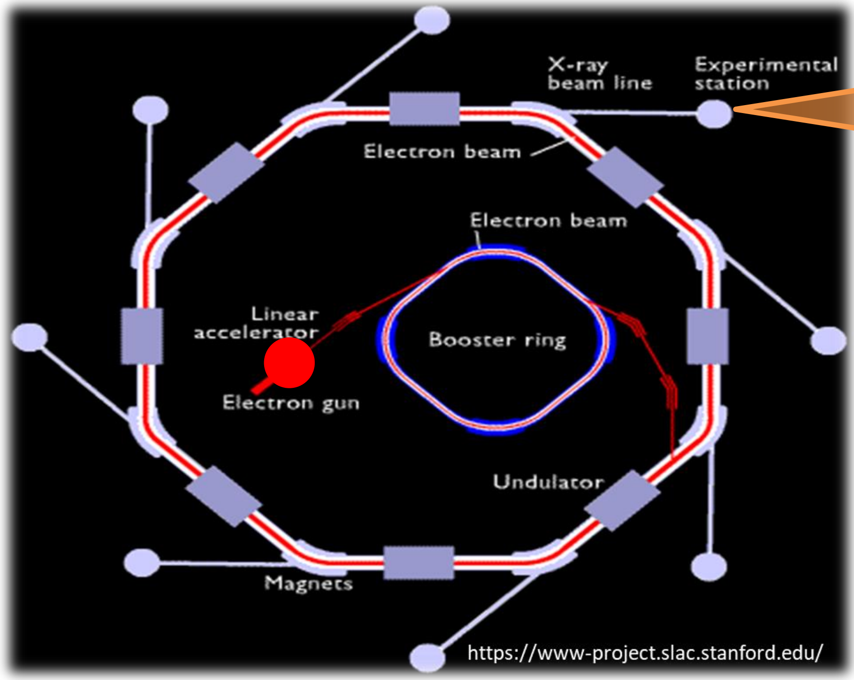
Iris H.Valido

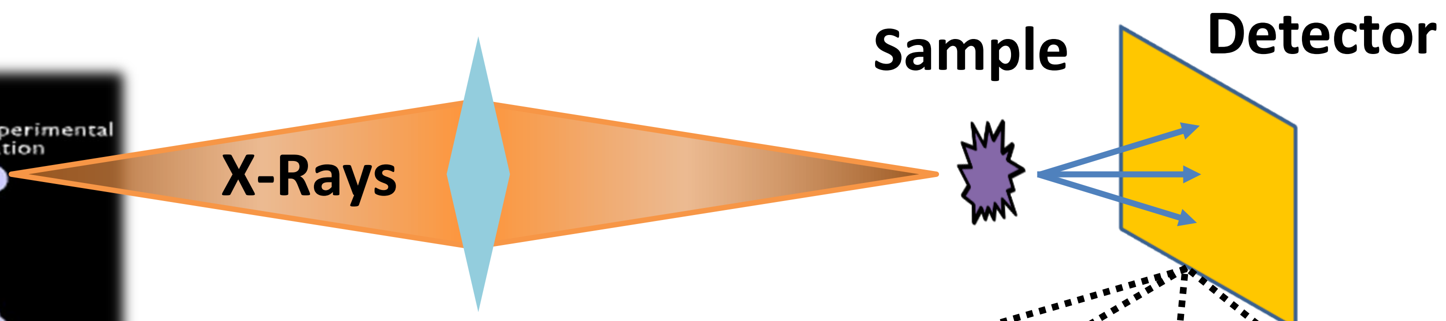
An overview of the synchrotron radiation techniques: Index

- Brief Introduction
- Spectroscopy
- Scattering
- Imaging



An overview of the synchrotron radiation techniques: Brief introduction





Energy	**Momentum**	**Positon**	**Dynamics**
↓	↓	↓	↓
Spectroscopy	***Scattering***	***Imaging***	***Time-resolving***
XAS Fluorescence Spectromicroscopy	MAD SAC SAXS XMS Interferometry	Microscopy Tomography Phasing Litography	Diffraction Luminescence Spectroscopy Imaging

Experimental techniques?

https://photon-science.desy.de/research/students__teaching/primers/experimental_techniques/index_eng.html

An overview of the synchrotron radiation techniques: Brief introduction

Experimental techniques

Spectroscopy	01. Low-Energy Spectroscopy 02. Soft X-Ray Spectroscopy 03. Hard X-Ray Spectroscopy 04. Optics/Calibration/Metrology	⇒	Chemical Information
Scattering	05. Hard X-Ray Diffraction 06. Macromolecular Crystallography 07. Hard X-Ray Scattering 08. Soft X-Ray Scattering	⇒	Atomic structure
Imaging	09. Hard X-Ray Imaging 10. Soft X-Ray Imaging 11. Infrared Imaging 12. Lithography	⇒	Spatial distribution

An overview of the synchrotron radiation techniques: Spectroscopy

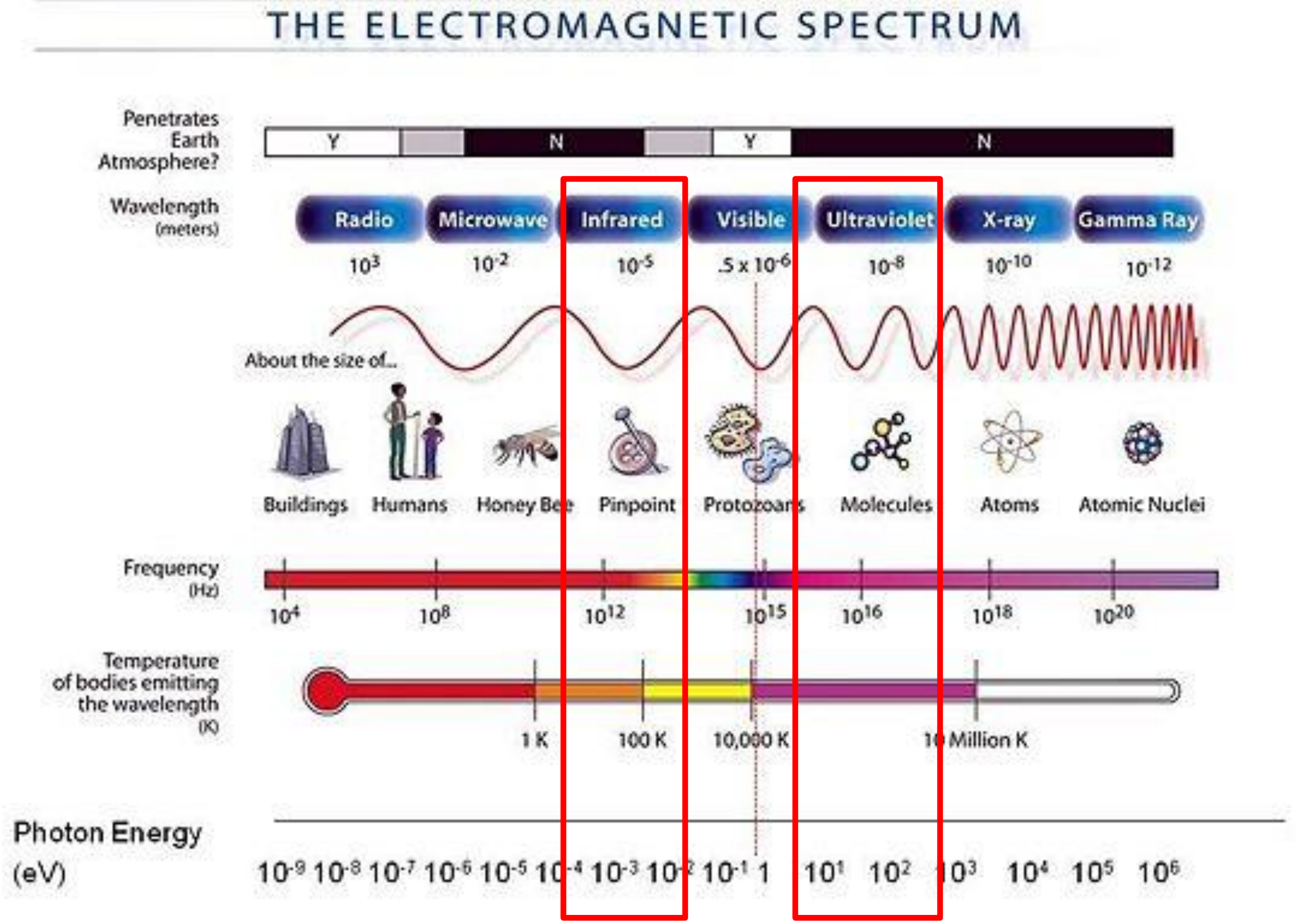
Spectroscopy	01. Low-Energy Spectroscopy 02. Soft X-Ray Spectroscopy 03. Hard X-Ray Spectroscopy 04. Optics/Calibration/Metrology

An overview of the synchrotron radiation techniques: Spectroscopy

__Spectroscopy__: 01. Low-Energy Spectroscopy

Radiation:
- UV region of the spectrum: 10-100 eV
- IR and Terahertz region: < 1 eV

depts.washington.edu



How it works:

The sample is illuminated with light (in the different spectral region, depending on the technique) and the product particles, which can be photons, electros, ions, atomic clusters, etc. are detected and analyzed.

An overview of the synchrotron radiation techniques: Spectroscopy

Spectroscopy: 01. Low-Energy Spectroscopy

Purpose:

- **UV**: elucidation of bonding in solids, surfaces and molecules; investigation of electron-electron correlations in solids, atoms and ions; and studying reaction pathways in chemical dynamics
- **IR**: study the activation of vibrational and other modes of excitement of atomic bonds.
- **Terahertz radiation**: since it is non-ionizing, it does not damage tissues, which makes it useful for the study of biological systems.

Typical applications:

- Complex materials
- Surfaces, clusters
- Atomic & molecular physics, astrophysics
- Combustion, chemical dynamics
- Biological systems

An overview of the synchrotron radiation techniques: Spectroscopy

Spectroscopy: 01. Low-Energy Spectroscopy

Includes:

- Vacuum-ultraviolet (VUV) spectroscopy
- Photoelectron spectroscopy (PES)
- Angle-resolved photoelectron spectroscopy (ARPES)
- Photon-ion spectroscopy
- Infrared (IR) spectroscopy
- Terahertz (THz) spectroscopy
- Ultraviolet photoemission spectroscopy (UPS)
- Cold-targed recoil-ion momentum spectroscopy (COLTRIMS)
- Photoelectron-photoion coincidence (PEPICO) spectroscopy
- Fourier transform infrared (FTIR) spectroscopy

Why synchrotron?:

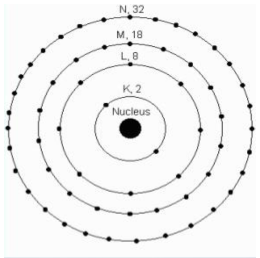
- High signal to noise (S/N) ratio with very high resolving power
- Its high brightness and possibility to achieve small spot sizes for analysis

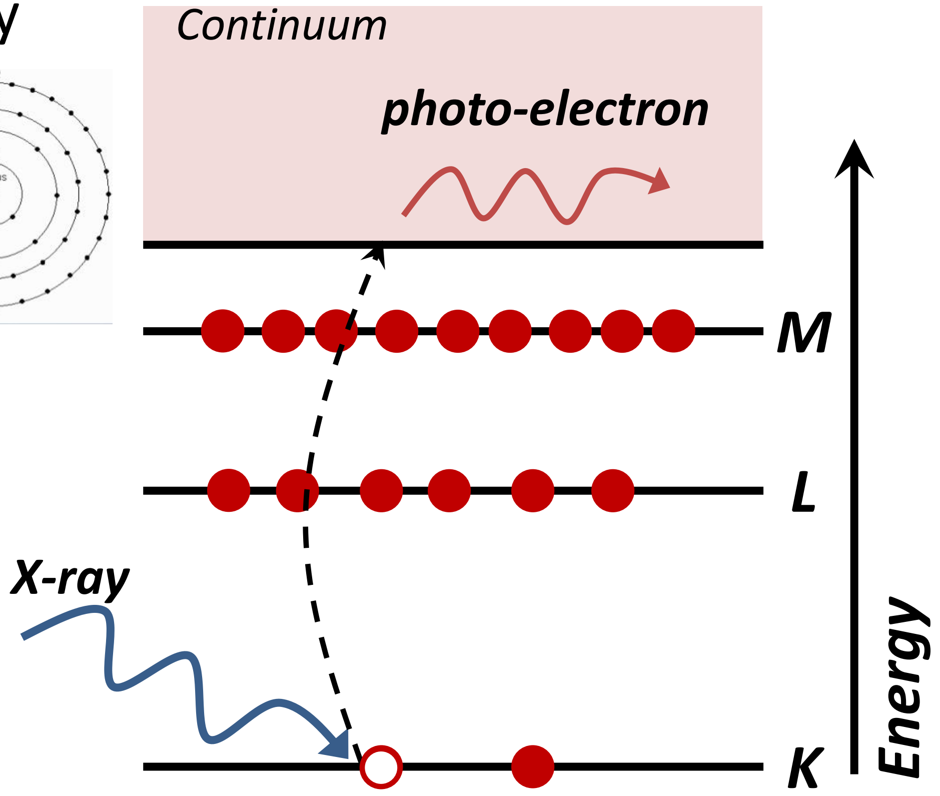
An overview of the synchrotron radiation techniques: Spectroscopy

<u>Spectroscopy</u>: 02. Soft X-Ray Spectroscopy

<u>How it works:</u>

In a basic and summarize level, the absorption, transmission, or reflectivity of a sample is measured as a function of photon energy





An atom will absorb an X-ray when the energy is transferred to a core-level electron, and it is ejected from the atom.

The atom is then excited with an empty electronic level (core hole).

The excess of energy form the X-ray is given to the ejected photo-electron

An overview of the synchrotron radiation techniques: Spectroscopy

Spectroscopy: 02. Soft X-Ray Spectroscopy

Purpose:

Soft X-Ray Spectroscopies employ the excitation of electrons in relatively shallow core levels (100-2000 eV) to probe the electronic structure of various kinds of matter

Typical applications:

- Complex materials
- Magnetic materials
- Environmental science, wet samples at ambient pressure
- Catalysis

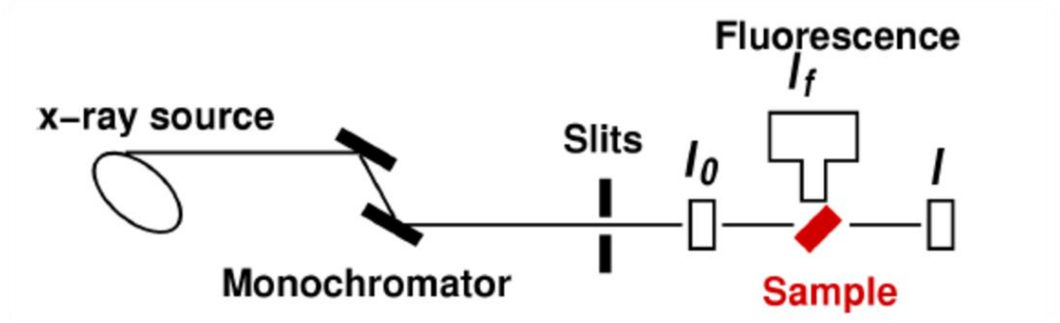
Includes:

- X-ray absorption spectroscopy (XAS)
- Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy
- X-ray magnetic circular dichroism (XMCD)
- Soft X-ray emission spectroscopy (SXES)
- X-ray photoemission spectroscopy (XPS)
- Auger spectroscopy

An overview of the synchrotron radiation techniques: Spectroscopy

<u>*Spectroscopy*</u>: 03. Hard X-Ray Spectroscopy

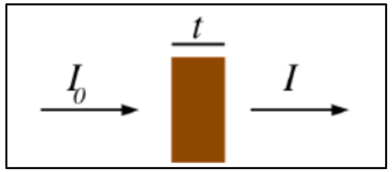
<u>How it works:</u>



μ depends strongly on x-ray energy E atomic number Z, and also on density ρ and Atomic mass A:

$$\mu \approx \frac{\rho Z^4}{AE^3}$$

- **Transmission:** measure what is transmitted through the sample: $I = I_0 e^{-\mu(E)t}$

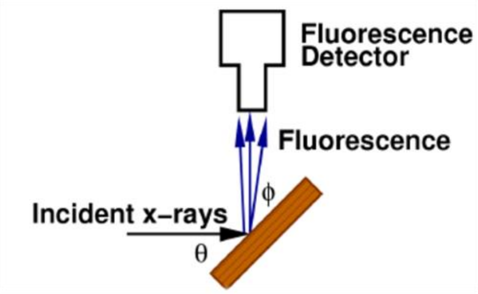


  Appropriate for concentration samples ≥10 wt.%.

- **Fluorescence:** measure fluorescent x-rays from the re-filling of the core hole: $\mu(E) \propto I_f / I_0$

  Appropriate for dilute elements ≤ 2 wt.%.

We need a measurement of μ(E) to ~0.1%, but with an energy tunable x-ray source, the measurements are fairly easy



An overview of the synchrotron radiation techniques: Spectroscopy

Spectroscopy: 03. Hard X-Ray Spectroscopy

Purpose:

Investigate geometric and electronic structures. The method is element-, oxidation-state, and symmetry-specific

Typical applications:

- Characterization of new and promising materials
- Elucidation of dilute chemical species of environmental concern

Includes:

- X-ray absorption spectroscopy (XAS)
  - Extended X-ray absorption fine structure (EXAFS) spectroscopy
  - X-ray absorption near-edge structure (XANES) spectroscopy
- Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy
- X-ray magnetic circular dichroism (XMCD)

An overview of the synchrotron radiation techniques: Spectroscopy

Spectroscopy: 04. Optics/Calibration/Metrology

Purpose:

Calibration of optical components used for X-ray detection, imaging, and spectroscopy as diagnostics. It is important for synchrotron radiation facilities to have some beamline(s) dedicated to the testing and calibration of optics and detectors for use on other beamlines

Typical applications:

- Nuclear physics (fusion plasma) diagnostics
- Astronomical spectroscopy and imaging, including remote detection of X-rays
- Synchrotron diagnostics and testing of beamline optical components
- Measurement and verification of X-ray optical data

An overview of the synchrotron radiation techniques: Scattering

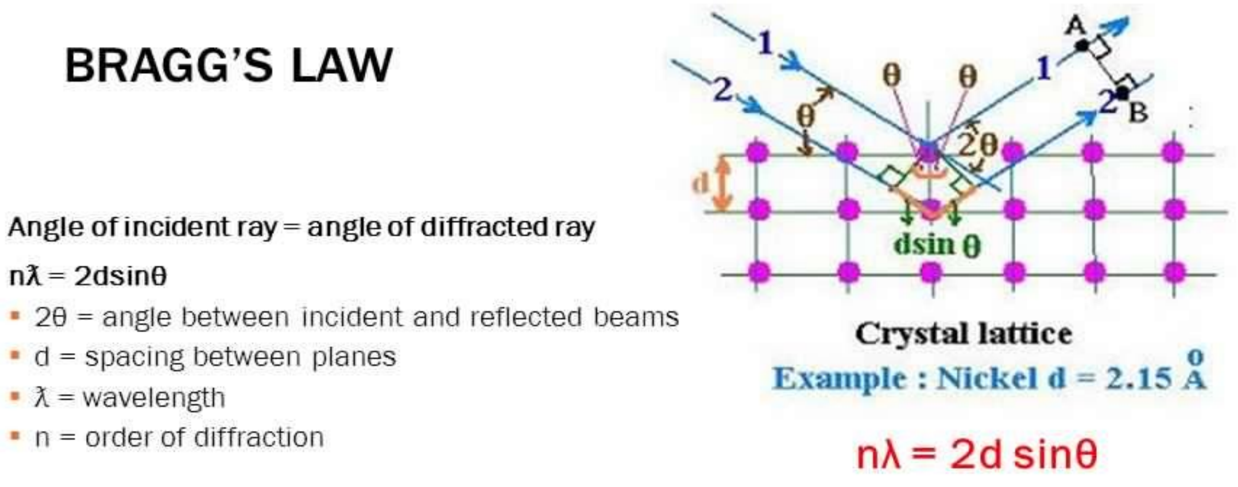
Scattering	05. Hard X-Ray Diffraction 06. Macromolecular Crystallography 07. Hard X-Ray Scattering 08. Soft X-Ray Scattering

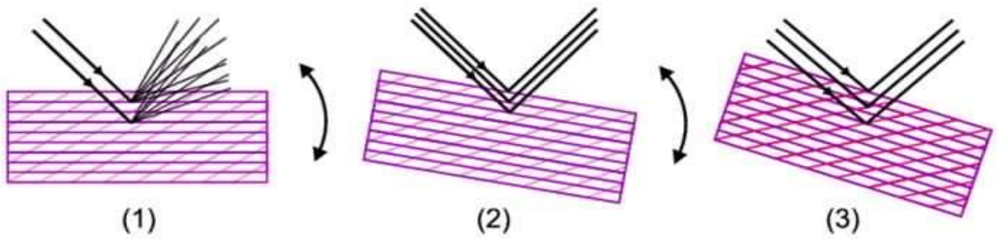
An overview of the synchrotron radiation techniques: Scattering

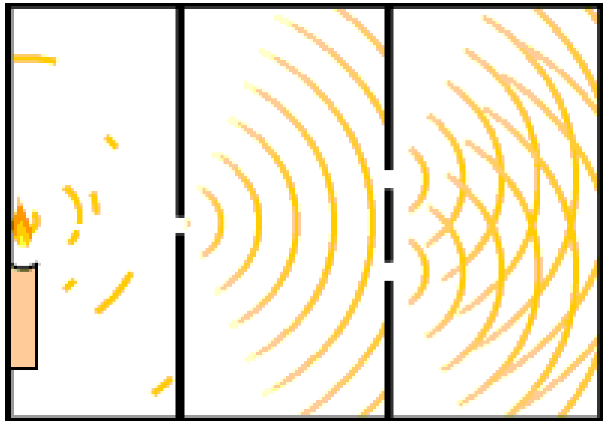
Scattering: 05. Hard X-Ray Diffraction

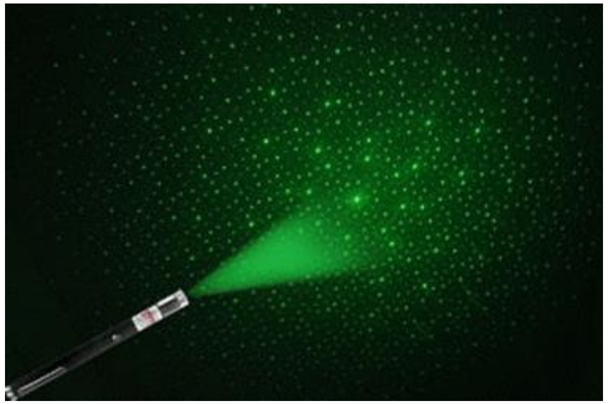
How it works:

X-rays are scattered (diffracted) into very specific directions when illuminating a crystalline sample









An overview of the synchrotron radiation techniques: Scattering

Scattering: 05. Hard X-Ray Diffraction

Purpose:

Determination of the atomic structure of materials

Typical applications:

- Structural studies of crystalline materials
- Drug design by pharmaceutical industry
- Biomineralization
- New microporous materials including natrolites, phosphates, and titanates
- Novel complex oxides: structure-property relationships, phase transitions
- Residual stress determination *in situ*

Includes:

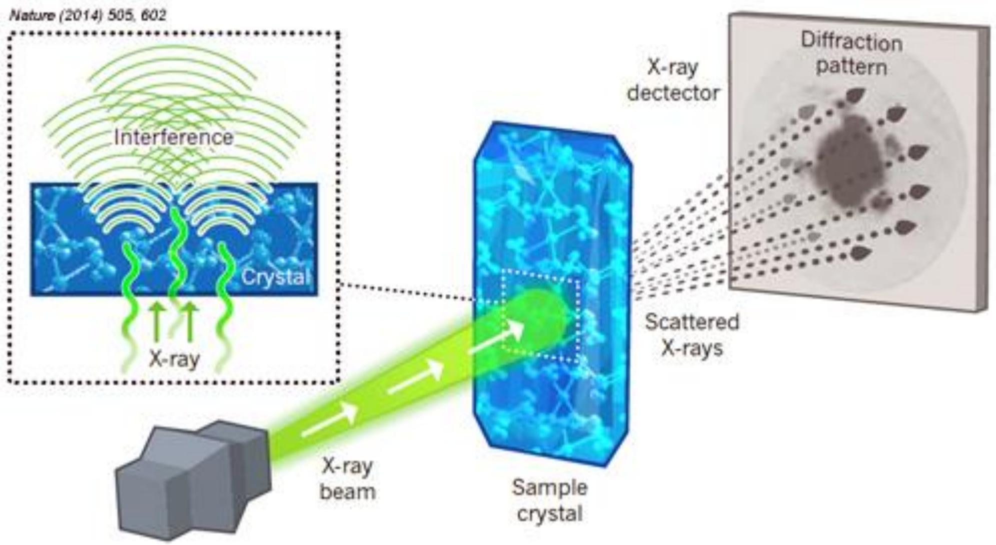
- X-ray diffraction (XRD):
  - powder, single-crystal, and surface diffraction
- X-ray standing wave (XSW)

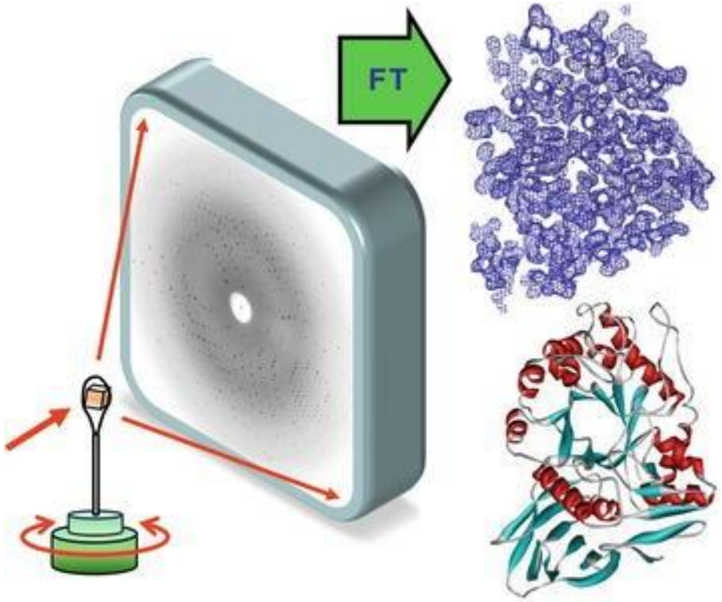
An overview of the synchrotron radiation techniques: Scattering

Scattering: 06. Macromolecular Crystallography

How it works:

X-rays are scattered (diffracted) into very specific directions when illuminating a crystalline sample





https://www.xtal.iqfr.csic.es/
Rupp, B. (2013). Macromolecular Crystallography: Overview. 10.1007/978-3-642-16712-6_655

An overview of the synchrotron radiation techniques: Scattering

Scattering: 06. Macromolecular Crystallography

Purpose:

Determination of the three-dimensional structure of large biological molecules

Typical applications:

- Therapeutic drug design
- Enzyme mechanisms
- Supramolecular structure
- Molecular recognition
- Nucleic acids
- Structural genomics
- High-throughput crystallography

Includes:

- Protein crystallography (PX)

An overview of the synchrotron radiation techniques: Scattering

Scattering: 07. Hard X-Ray Scattering

How it works:

When a sample is illuminated by x-rays, these incident x-rays can be deflected and scattered by the sample, producing complex patterns. Analysis of these patterns, their intensities as well as the angle of scatter (incident vs scattered x-rays), changes in polarization, wavelength, and/or energy, can reveal structural, elemental and atomic information about the sample. There are two principal variants:

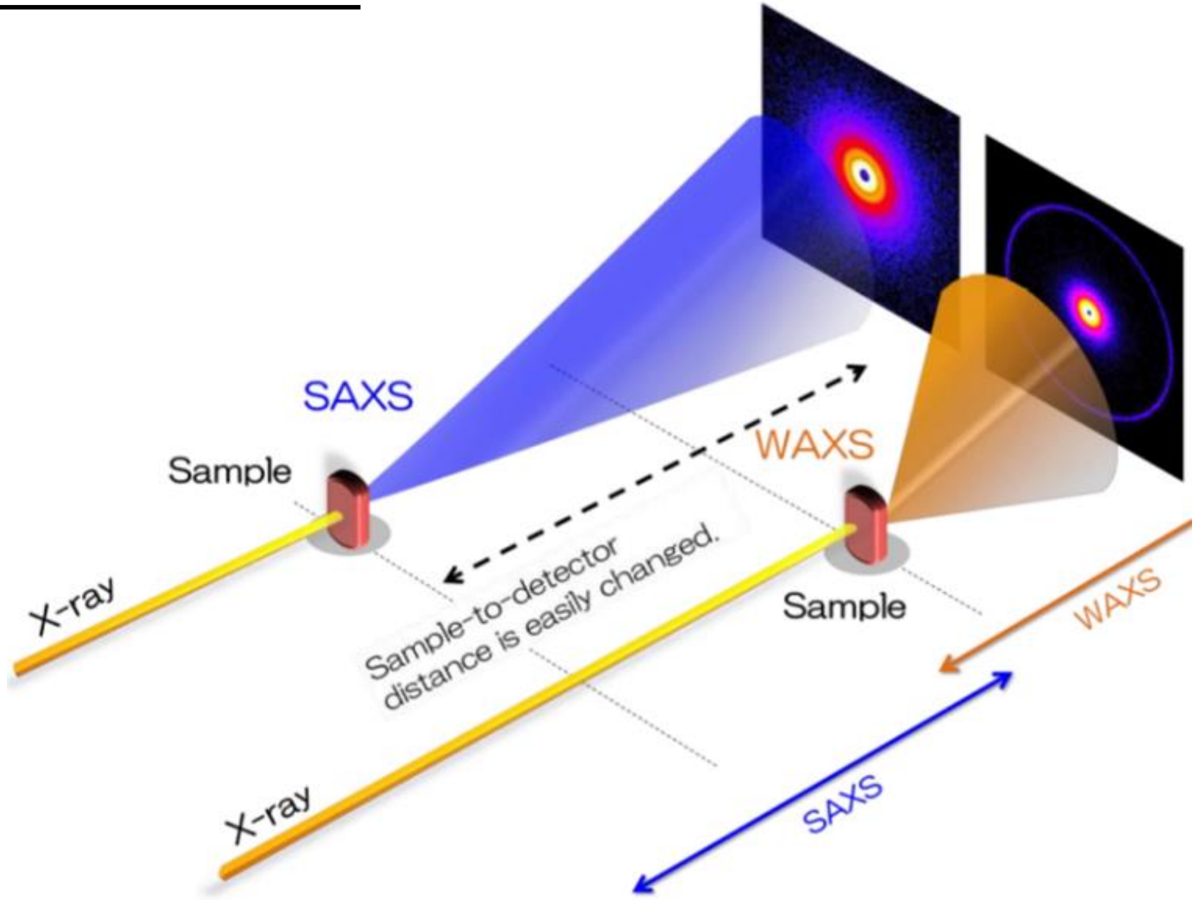
- Elastic: the energy (wavelength) of the detected X-ray is the same as that of the incident X-ray
- Inelastic: the energy of the detected X-ray is lower than that of the incident X-ray. The lost of energy is carried away by a vibrational, electronic, or magnetic excitation. The detection system in this case requires a spectrometer to measure the energy loss

https://www.princetoninstruments.com/learn/x-ray-scattering/intro-to-x-ray-scattering
Experimental Techniques at Light-Source Beamlines – U.S. Synchrotron Radiation Light Sources

An overview of the synchrotron radiation techniques: Scattering

__Scattering__: 07. Hard X-Ray Scattering

<u>How it works:</u>



https://www.princetoninstruments.com/learn/x-ray-scattering/intro-to-x-ray-scattering
Courtesy of Marc Malfois (SAXS Workshop 2014, ALBA)

An overview of the synchrotron radiation techniques: Scattering

Scattering: 07. Hard X-Ray Scattering

Purpose:

Measures the patterns, intensities, and angles of scatter produced when a sample is illuminated by a monochromatic X-ray beam. Information on shape, dispersity, sample size, porosity, morphology, and orientation are some of the few things that can be measured via X-ray scattering

Typical applications:

- Liquid-vapor, liquid-liquid, and molecular film interfaces
- Colloids, solution-phase protein, polymers
- Collective dynamics in soft materials
- Short-range order in amorphous materials
- Phonons and elementary excitation in solids
- Electron momentum distribution in solids

Experimental Techniques at Light-Source Beamlines – U.S. Synchrotron Radiation Light Sources
princetoninstruments.com/learn/x-ray-scattering

An overview of the synchrotron radiation techniques: Scattering

Scattering: 07. Hard X-Ray Scattering

Includes:

- Small-angle X-ray scattering (SAXS)
- Wide-angle X-ray scattering (WAXS)
- Grazing-incidence small-angle X-ray scattering (GISAXS)
- X-ray Raman scattering
- Compton scattering
- Inelastic X-ray scattering (IXS)
- Resonant inelastic X-ray scattering (RIXS)
- Nuclear resonant scattering (NRS)
- X-ray photon correlation spectroscopy (XPCS)

An overview of the synchrotron radiation techniques: Scattering

Scattering: 08. Soft X-Ray Scattering

How it works:

It is a photon-in/photon-out technique.

Purpose:

Soft x-ray scattering techniques employ the excitation of electrons in relatively shallow core energy levels (100–2000 eV) to probe the electronic structure and other properties of various kinds of matter

Typical applications:

- Strongly correlated materials
- Magnetic materials
- Environmental science
- Catalysis

An overview of the synchrotron radiation techniques: Scattering

Scattering: 08. Soft X-Ray Scattering

Includes:

- Soft X-ray emission spectroscopy (SXES)
- Inelastic X-ray scattering (IXS)
- Resonant X-ray inelastic scattering (RIXS)
- Speckle patterns
- Small-angle X-ray scattering (SAXS)

An overview of the synchrotron radiation techniques: Imaging

Imaging	09. Hard X-Ray Imaging 10. Soft X-Ray Imaging 11. Infrared Imaging 12. Lithography

An overview of the synchrotron radiation techniques: Imaging

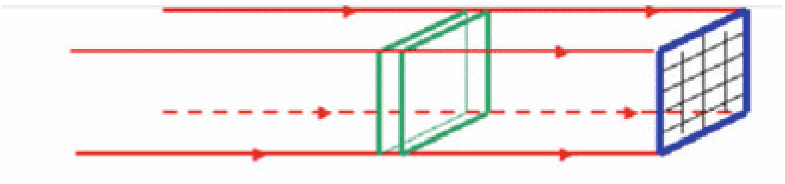
Imaging: 09. Hard X-Ray Imaging

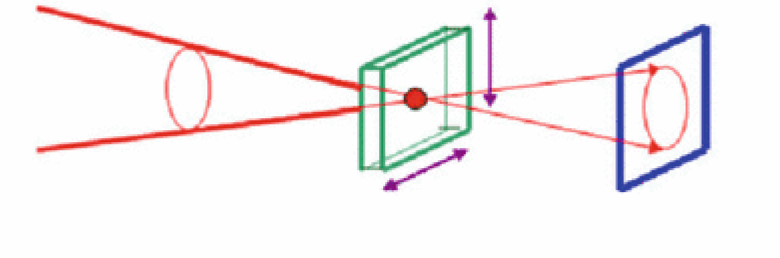
How it works:

There are two basic experimental methods:

- Imaging: a full-field image can be recorded with a parallel beam with a pixelated detector (each pixel correspond to a given volume in the sample). The spatial resolution of the image is associated with the pixel size.
- Scanning: a very small illuminated spot is created on the sample using focusing devices. The image is then built up by “raster scanning” the sample through the illuminated spot

In either case, there has to be a physical cause of the contrast. This can be due to changes in absorption, elemental composition, or refractive index of the sample.





Synchrotron Radiation, Basics, Methods and Applications Editors: Settimio Mobilio

An overview of the synchrotron radiation techniques: Imaging

Imaging: 09. Hard X-Ray Imaging

Typical applications:

- Human and animal physiology
- Mapping of magnetic domains in two dimensions
- Mapping of composite materials in three dimensions (tomography)
- Properties of individual grains in a polycrystalline material
- Mapping of the distribution of elements in cells
- Strains in near-perfect crystals
- Time-resolved imaging of sprays

Includes:

- Radiography
- Phase contrast imaging
- Scanning micro/nanoprobe
- Fullfield microscopy
- Diffraction enhanced imaging (DEI)
- X-ray tomography
- Topography

An overview of the synchrotron radiation techniques: Imaging

Imaging: 10. Soft X-Ray Imaging

How it works:

Employs photons or electron optics to achieve the necessary high resolution

Purpose:

The wavelengths of soft X-ray photons (1-15 nm) are very well suited to probe the interior structure of biological cells and inorganic mesoscopic systems. For example, cell biology uses radiation around 300-500 eV, while nanomagnetic studies need 600-900 eV

Typical applications:

- Cell biology
- Nanomagnetism
- Environmental science
- Soft matter, polymers

An overview of the synchrotron radiation techniques: Imaging

Imaging: 10. Soft X-Ray Imaging

Includes:

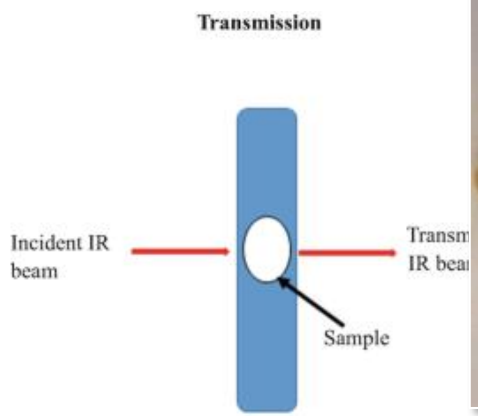
- Soft X-ray imaging
- Photoelectron emission microscopy (PEEM)
- Scanning transmission X-ray microscopy (STXM)
- Full-field microscopy
- X-ray diffraction imaging (XDI)
- X-ray tomography
- Computer-aided tomography (CAT) scans

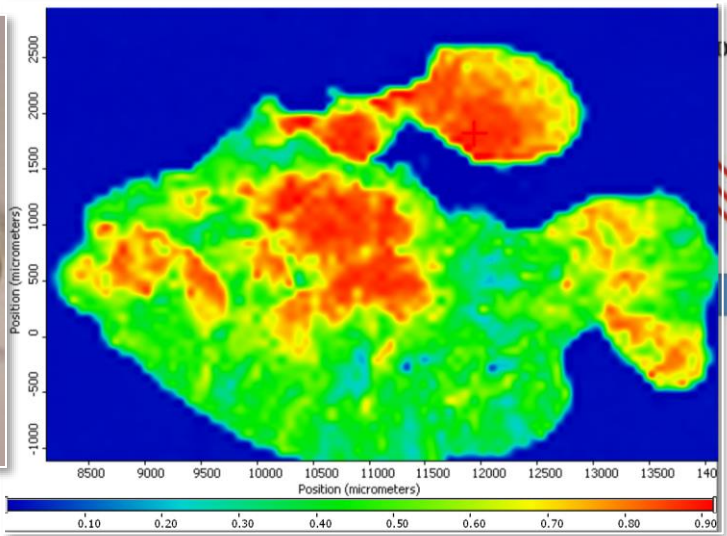
An overview of the synchrotron radiation techniques: Imaging

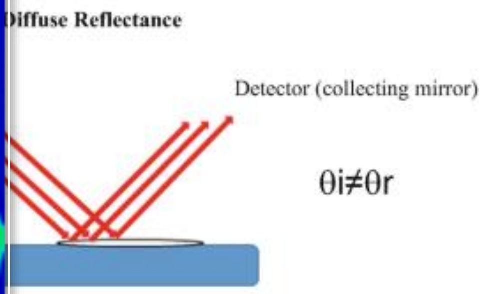
<u>Imaging</u>: 11. Infrared Imaging

<u>How it works:</u>

IR synchrotron radiation is focused through, or reflected from, a small spot on the specimen and then analyzed using a spectrometer. Tuning to characteristic vibrational frequencies (obtained in the analyzed spectra) serves as a sensitive fingerprint for molecular species. Then, images of the various species are built up by raster scanning the specimen through the small illuminated spot.







Abidi, N. (2021). Introduction to FTIR Microspectroscopy. In: FTIR Microspectroscopy . Springer, Cham. https://doi.org/10.1007/978-3-030-84426-4_1

An overview of the synchrotron radiation techniques: Imaging

Imaging: 11. Infrared Imaging

Typical applications:

- Chemistry in biological tissues
- Chemical identification and molecular conformation
- Environmental biodegradation
- Mineral phases in geological and astronomical specimens
- Electronic properties of novel materials
- Forensic studies

Includes:

- Infrared (IR)
- Microspectroscopy
- Infrared imaging
- Infrared microprobe

An overview of the synchrotron radiation techniques: Imaging

Imaging: 12. Lithography

How it works:

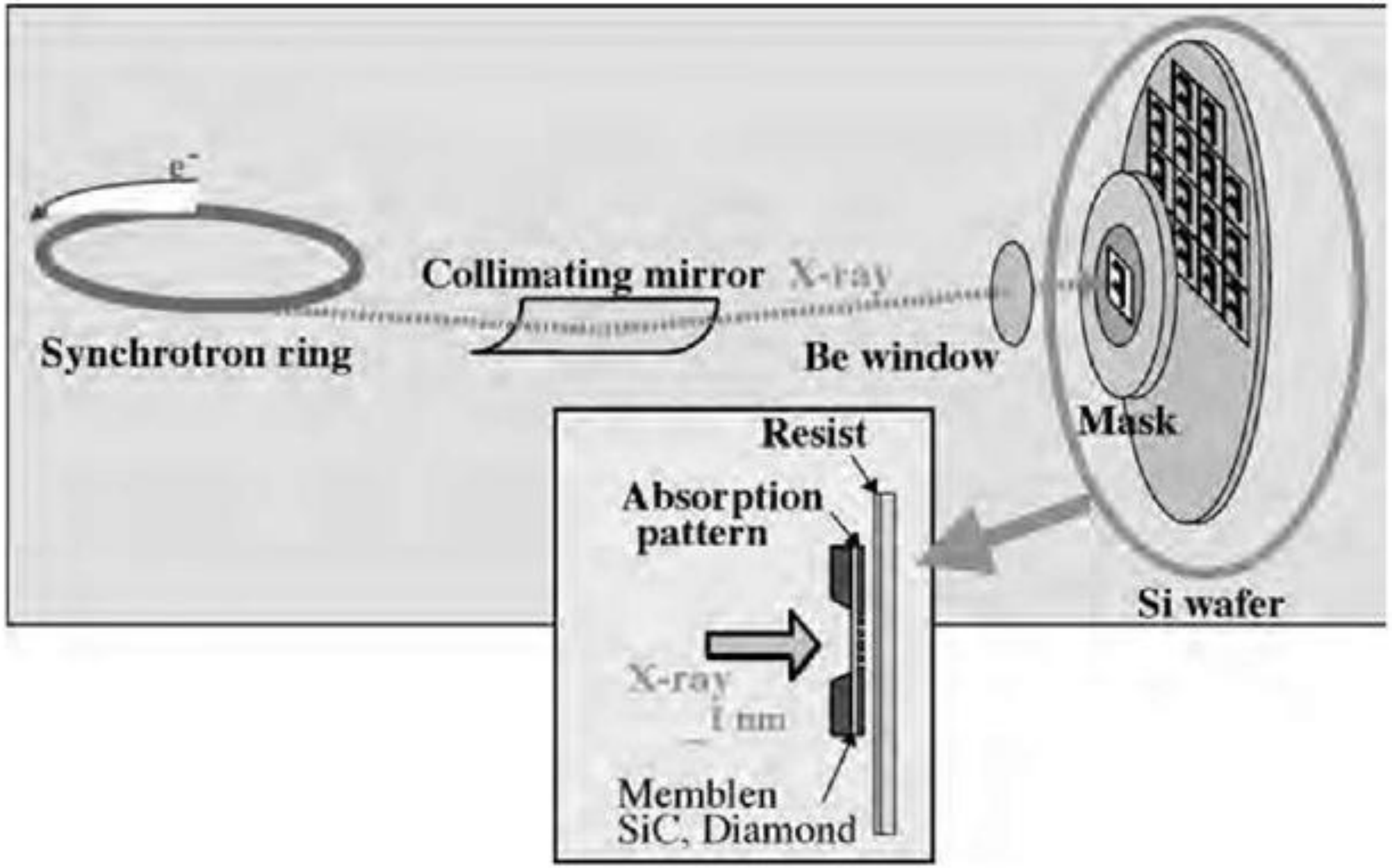
X-ray lithography (XRL) is an advanced version of optical lithography in which shorter wavelengths are used. A special type of mask is used with different local X-ray absorption areas to define the patter. Then, this pattern is replicated on an X-ray sensitive material called a resist, which was previously deposited on a substrate. When the X-ray passing throygh the pattern falls on the resist, it may cause cross-linking (for negative resists) or bond breaking (for positive resists), depending on the chemical nature of the resist. After exposure, the whole thing is dipped in a specific solvent to reveal the patter. This is how X-ray lithography creates nanopatterns on the substrate

T. Mahbub, et al. (2020). Chapter 1 - Introduction to nanomaterials and nanomanufacturing for nanosensors. *Nanofabrication for Smart Nanosensor Applications. 10.1016/B978-0-12-820702-4.00001-5*

An overview of the synchrotron radiation techniques: Imaging

Imaging: 12. Lithography

How it works:



http://what-when-how.com/nanoscience-and-nanotechnology/nanolithography-length-scale-limitations-part-2-nanotechnology/

An overview of the synchrotron radiation techniques: Imaging

Imaging: 12. Lithography

Includes:

- Extreme ultraviolet (EUV) lithography
- Interferometry
- LIGA (lithography, electroplating and molding)
- Microelectromechanical structures (MEMS)
- X-ray lithography
- Nanolithography

microchip

TUNTWIN’s Workshop

شكرا

Merci!

Thank you!

¡Gracias!

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