X-Ray Photoelectron Spectrometry (XPS)
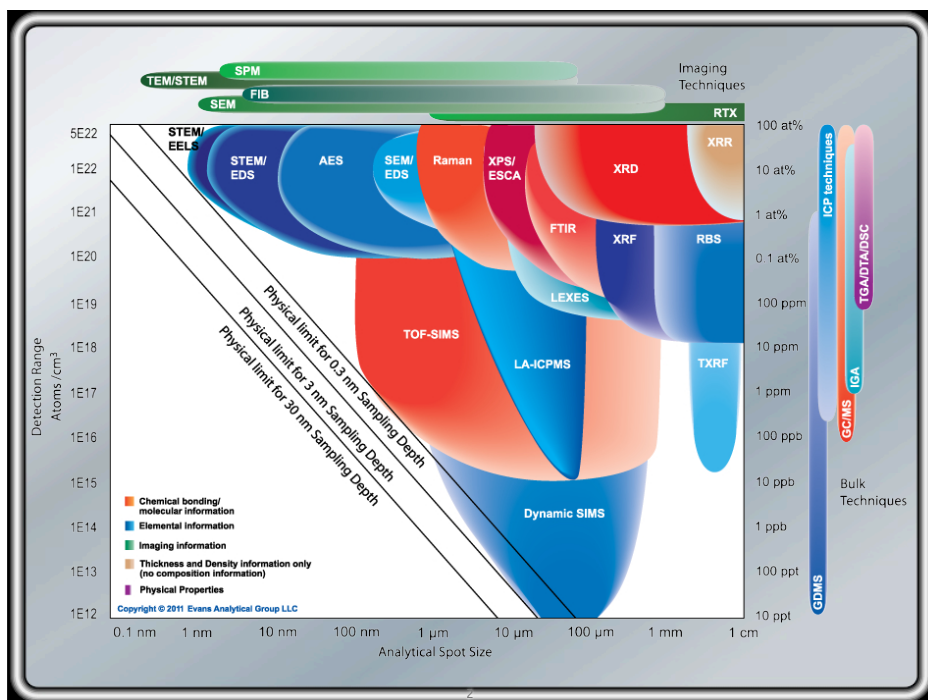
Electron Spectroscopy for Chemical Analysis (ECSA)
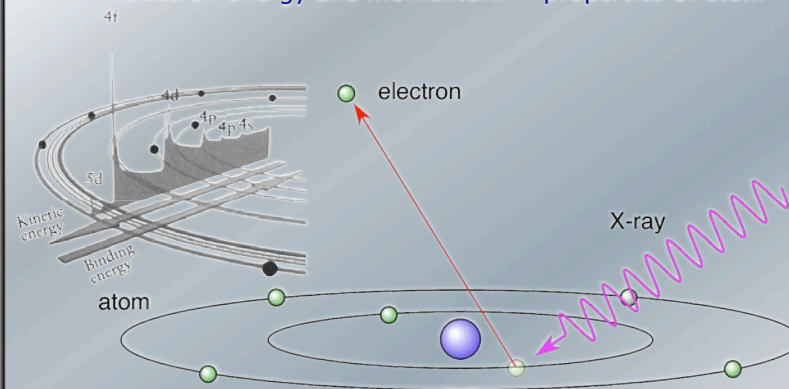

Comparison of Surface Analysis Techniques

	AES	XPS	TOF-SIMS	D-SIMS
Probe Beam	Electrons	Photons	Ions	Ions
Analysis Beam	Electrons	Electrons	Ions	Ions
Spatial Resolution	0.006 μm	2-30 μm	0.10 μm	1 μm
Sampling Depth(Å)	5-75	5-75	1-10	1-10
Detection Limits	0.1atom %	0.01atom %	1ppm	1ppb
Information Content	Elemental	Elemental Chemical	Elemental Chemical Molecular	Elemental
Depth Profile Speed	1 μm / hr	0.5 μm / hr	1 μm / hr	10 μm / hr
Quantification Good	Acceptable	Excellent	Std. needed	

Principle of XPS

- photon in, electron out

- electron energy and momentum $\Rightarrow$ properties of atom

Brief History of XPS

1905 quantum-mechanical explanation of the photoelectric effect (Einstein, Nobel Prize 1921)

1923 photoionization experiments (Robinson)

1930 first experiments of electron energy-loss spectroscopy (Rudberg)

1949 first electron lenses (Möllenstedt, Boersch)

1950s first successful studies in the field of photoelectron spectroscopy (Siegbahn)

1960s first electrostatic energy analyzers (Powell) essential to prepare quantitative evaluation

1981 Nobel Prize for Siegbahn

Photoelectric Effect

- emission, or ejection, of electrons from the surface of a metal in response to incident light (→"photo-electrons")

- classical Maxwell wave theory of light:
  energy of the ejected electrons ⇔ light intensity

- Lenard: NO!

- Einstein (1905): light ⇔ "photons" with energy

$$E = h\nu$$

E: Energy; h: Planck constant; ν: frequency of the corresponding light wave.

- photo–electric process → direct *signature* of interaction between photon and atom
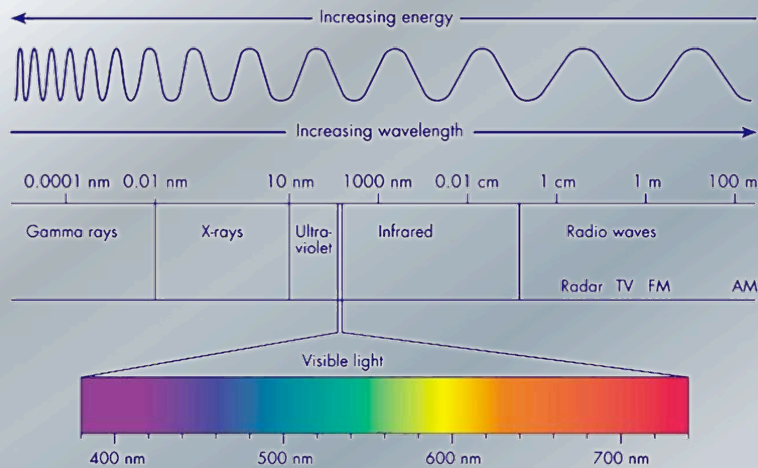

X-Ray Photoelectron Spectroscopy

- synonym for XPS:
  Electron Spectroscopy for Chemical Analysis (ESCA)

Basic Idea of XPS

- measure $E, \boldsymbol{p}$ of photo-electrons

- infer properties (e. g. Z) of emitting atom

- works because
  - on absorption, incident photon transfers its *entire* energy to a bound electron
  - ⇒ energy of the photoelectron ↔ binding energy of the electron in the target atom
  - ⇒ energy of the photoelectron ↔ chemical identity of atom that absorbed the photon

- identification of elements ⇐ measurement of the energy of the electrons that escape without energy loss

Spectrum of Electromagnetic Waves

Instrumentation

⇒ photoelectron spectroscopy requires

- ultra-high vacuum
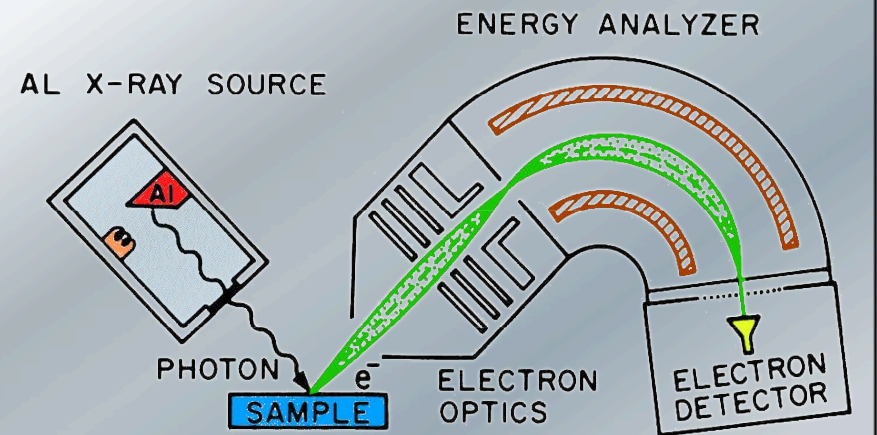- monochromatic photon source
- electron spectrometer

• X-ray sources for XPS

- best: synchrotron
  · bright
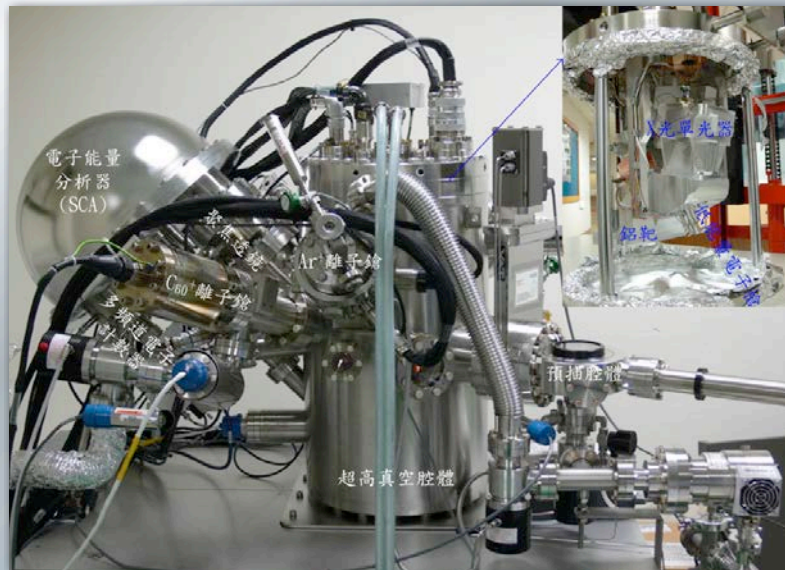 · tunable
  · polarized
- but: most expensive

Photoelectric Effect

- practice: $E = 10\,\text{eV} \ldots 0.1\,\text{MeV}$
- low-energy photons – ultra-violett light (→UPS)
  - ↔ outermost, less tightly bound electrons
  - outermost electrons are involved in chemical bonding, not associated with specific atoms
  - less important for chemical analysis
- high-energy photons – soft X-rays (→XPS)
  - penetrate deep into the atoms
  - interact with inner-shell electrons ⇒ chemical analysis
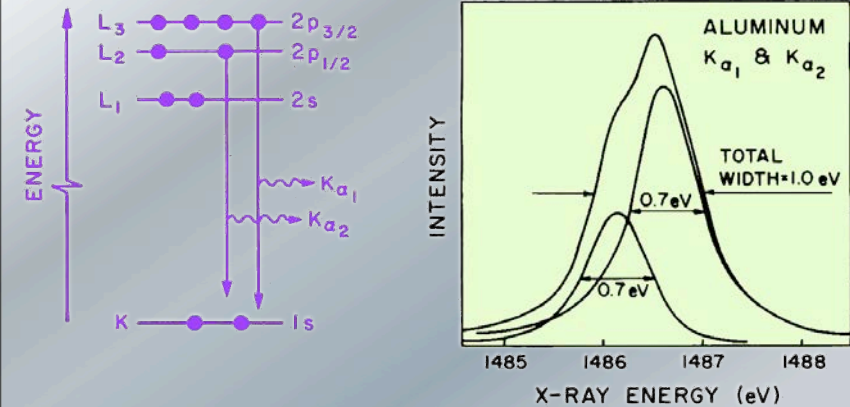 - escape depth of photoelectrons:
  - only $1 \ldots 2\,\text{nm}$ (!)

Basic XPS Apparatus

PHI 5000 VersaProbe SXM at Sinica (2007/6/18)

Al as X-ray Source

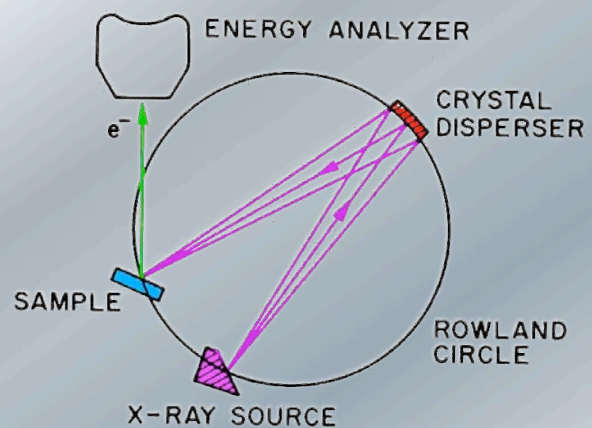## Radiation Sources

- typical laboratory source:
  - Mg or Al target
  - bombarded by electrons
  - Mg, Al $\Rightarrow$ soft X-rays
  - about 50 %: K_α
  - Bremsstrahlung relatively less important than for hard X-rays (e. g. Cu)
    - · width of characteristic peaks: ≈ 1 eV
    - · Bremsstrahlung distributed over several keV
    - $\Rightarrow$ spectrum sufficiently "clean" for the purpose of surface analysis
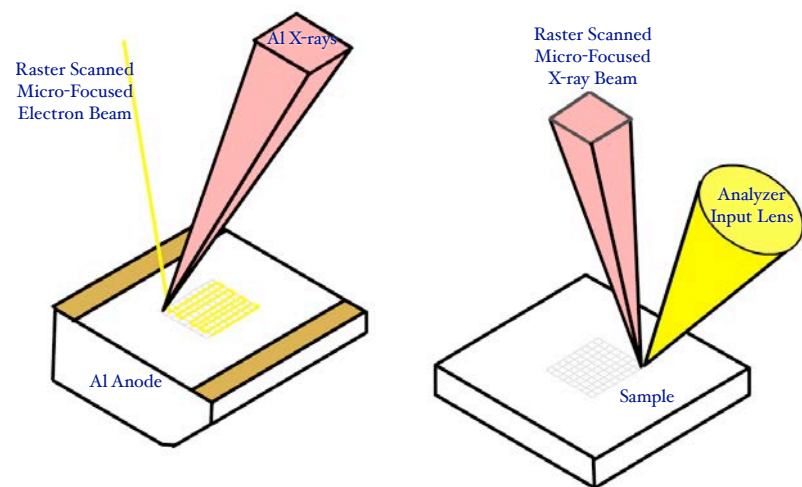
Radiation Sources

- Al $K_{\alpha_{1,2}}$ lines consist of two components, separated by 0.4 eV spin–orbit splitting of the 2p state

- somewhat better resolution is obtained with Mg K_α (≈ 0.8 eV)

- compare K_α lines of Cr (at ≈ 5 keV) and Cu (at ≈ 8 keV): energy width ≥ 2.0 eV

- $\Rightarrow$ not suitable for high-resolution studies without further energy selection

- $\rightarrow$ light elements (Mg, Al) provide most suitable X-ray sources

- if still higher energy resolution required:
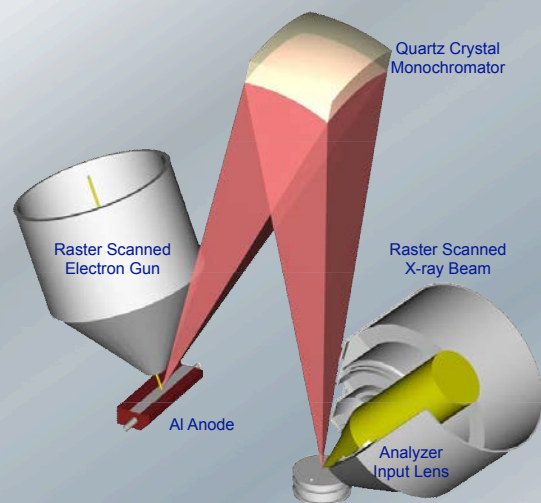 X-ray monochromator

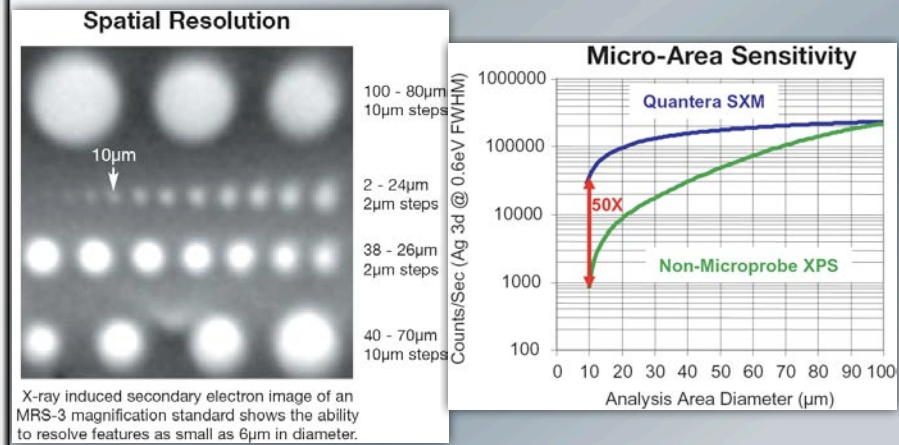# X-ray Monochromator

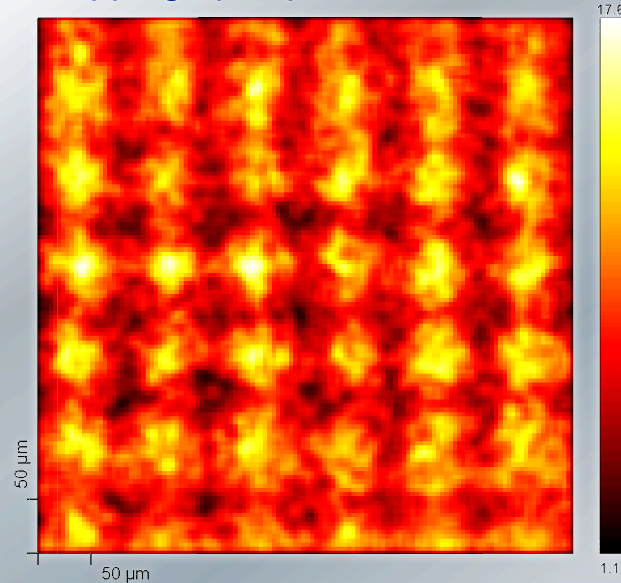# Micro-Focused X-ray Source

Scanning X-ray Microscopy

Spot Size of SXM

N1s Mapping of Self-Assembled Monolayer

Electron Spectrometers

- cylindrical mirror analyzer (CMA)
  - double pass CMA:
  → two CMAs in series
  - spherical retarding grids
    → scan spectrum while CMA is operated at constant pass energy
    → maintain constant energy resolution
    · deflection by potential difference between inner and outer cylinder line
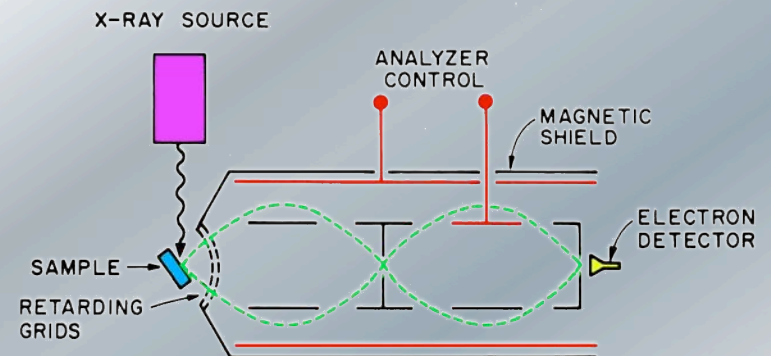   · potential difference set by analyzer control

Electron Spectrometers

- spectrometer ⇔ energy-dispersive ray path for electrons

- deflection in electrostatic or magnetic fields

- magnetic deflection analyzers are difficult to use in routine analysis

- most laboratory systems: electrostatic analyzers

- two different modes: deflection and reflection

- deflector: electrons travel *along* equipotential lines

- mirror: electrons travel *across* equipotential lines

- there several common types of analyzers

Double-Pass Cylindrical Mirror Analyzer

Electron Spectrometers

- hemispherical analyzer
  - two concentric hemispheres
  - ↔ spherical capacitor
  - voltage ⇒ radial electric field
  - → electrons on paths inclined to the central path are accelerated or decelerated
  - all electrons with the selected energy reach the exit aperture
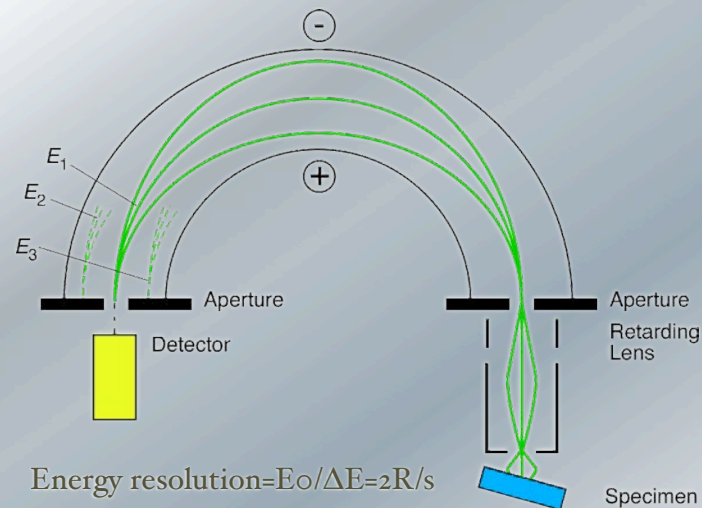 - ⇒ focusing in two dimensions (point-to-point imaging)
  - ⇒ efficient

Pass Energy

- the potential difference between inner and outer hemisphere of the analyzer
- same function as the energy selective slit at energy-dispersive plane
- with a smaller pass energy
  - ➡ higher energy resolution
  - ➡ less electrons can reach detector
    - · poor count
    - · poor signal-to-noise ratio
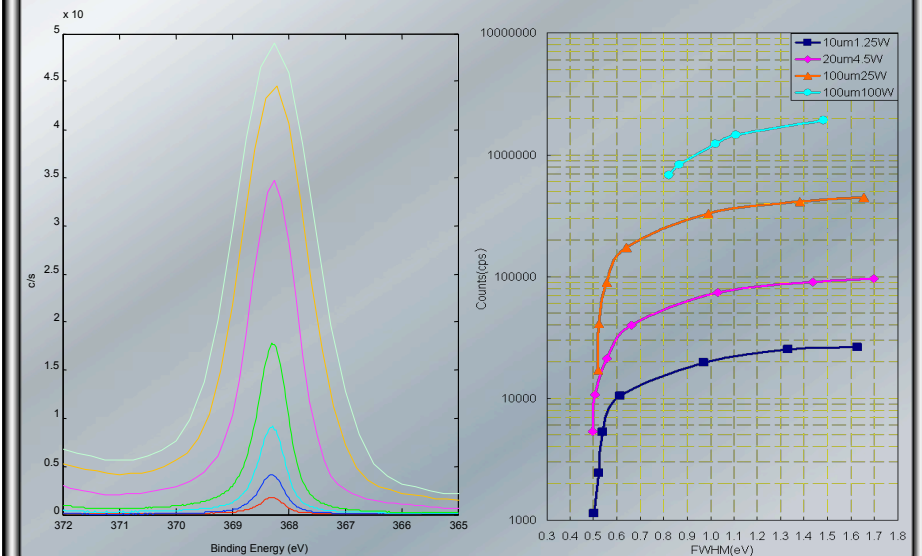 - ➡ need longer acquisition time for spectrum quality

Hemispherical Analyzer

E_1
E_2
E_3

Aperture
Detector
Aperture
Retarding Lens
Specimen

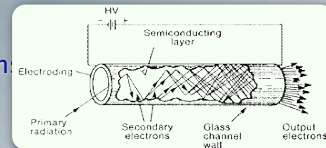Energy resolution = $E_0/\Delta E = 2R/s$

Effect of Pass Energy

Electron Spectrometers

- detection system
  - gain provided by electron multipliers
  - channel electron multiplier or channeltron
    - cone-like opening and continuous tube of high resistivity
    - semiconducting glass with high secondary emission
    - high electric field along the tube
    - incident electrons create a shower of secondary electrons
    - hit the tube walls
    - create further secondary electrons
    - a gain of 10^8 can be achieved

Kinetic Energy of Photoelectrons

- XPS: surface irradiated with photons of energy $h \cdot \nu = \hbar\omega$

- conservation of energy:
$$\hbar\omega + E_{tot}^i = E_{kin} + E_{tot}^f [k]$$

E_{tot}^i: total energy of the initial state; E_{kin}: kinetic energy of the photoelectron; E_{tot}^f: total final energy after ejection of the photoelectron from the k-th level.

- contributions from the recoil energy E_r are negligible (significant compared to the line width in XPS spectra only for light elements)

- binding energy of a photoelectron:
  energy required to remove it to infinity with zero kinetic energy

Retarding Lens

- high kinetic energy electrons
  - higher gain in channeltron
  - N(E) becomes EN(E)
    - need to normalize the intensity by N(E)/E
  - higher E_0
    - resolution change with energy
- retarding lens
  - slow electron down (dynamically scanned for the whole energy range)
  - fixed energy for analyzer and detector
  - fixed resolution and gain

Kinetic Energy of Photoelectrons

- binding energy of an electron in the k-th level referred to the local vacuum level: $E_V^B [k] = E_{tot}^f - E_{tot}^i$

- substituting
$$\hbar\omega + E_{tot}^i = E_{kin} + E_{tot}^f$$

yields the "photoelectric equation"
$$\hbar\omega = E_{kin} + E_V^B [k]$$
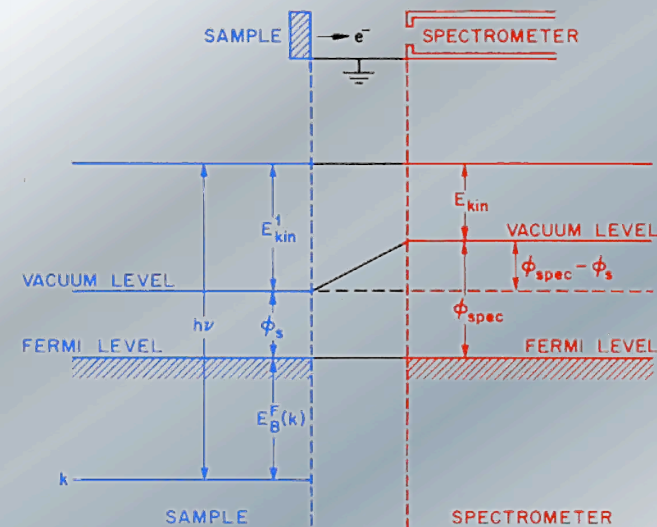
Binding Energy

- binding energies are expressed relative to reference level

  - gas: vacuum level

  - solids: Fermi level
    (electrical contact to the spectrometer)

- spectrometer and sample in thermodynamic equilibrium

$\Rightarrow$ Fermi levels are equal in both systems

- in passing from sample surface to spectrometer, the pho-
toelectron feels a potential difference

$$\Delta\phi = \phi_{\mathrm{spec}} - \phi_{\mathrm{s}}$$

ϕ_{spec}: work function of the spectrometer; ϕ_{s}: work function of the specimen.

Energy Levels of Metallic Specimens

Binding Energy

$\rightarrow$ energy levels of metallic specimens:

  - photoelectron energy: E_{kin}^{1} relative to vacuum level of the sample

  - the electron is detected in the spectrometer with a work function ϕ_{spec}

  - measured energy:

$$E_{\mathrm{kin}} = E_{\mathrm{kin}}^{1} + \left(\phi_{\mathrm{s}} - \phi_{\mathrm{spec}}\right)$$

$\rightarrow$ for metallic specimens, determine binding energy from

$$\hbar\omega = E_{\mathrm{B}}^{\mathrm{F}}[k] + E_{\mathrm{kin}} + \phi_{\mathrm{spec}}$$

$\hbar\omega$: photon energy;
$E_{\mathrm{B}}^{\mathrm{F}}[k]$: binding energy referred to the Fermi level.

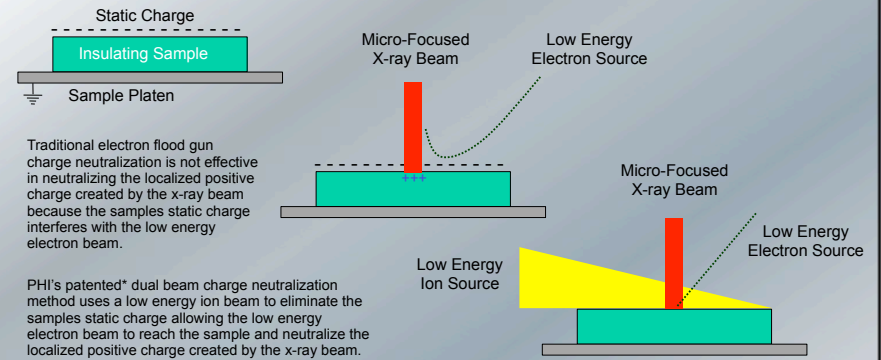## Universal Curve for Electron Mean Free Path Versus Energy

Binding Energy

→ the work function of the specimen is not involved, but that of the spectrometer is

- insulating samples
  - requires more care
  - charging
  - uncertainty about the location of the Fermi level in the band gap

- one approach:
  - deposit Au on the sample surface
  - use one of the known Au core levels to define the energy scale

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Dual Beam Charge Neutralization

Static Charge

Insulating Sample

Sample Platen

Traditional electron flood gun charge neutralization is not effective in neutralizing the localized positive charge created by the x-ray beam because the samples static charge interferes with the low energy electron beam.

PHI's patented* dual beam charge neutralization method uses a low energy ion beam to eliminate the samples static charge allowing the low energy electron beam to reach the sample and neutralize the localized positive charge created by the x-ray beam.

Micro-Focused X-ray Beam

Low Energy Electron Source

+++

Micro-Focused X-ray Beam

Low Energy Electron Source

Low Energy Ion Source

Binding Energy

- alternatively:
  - refer to a well-known feature of the XPS spectrum e. g.: valence band edge

- in the following, E_{B} denotes binding energy without explicitly specifying the reference level for the energy
  - metals → Fermi level
  - semiconductors, insulators: ambiguity, + charging
  - → care must be taken in evaluating such spectra

- example: Mg K$_\alpha$ ($E = 1.25\,\mathrm{keV}$) irradiation of Ni

- spectrum exhibits typical sharp peaks and extended tails

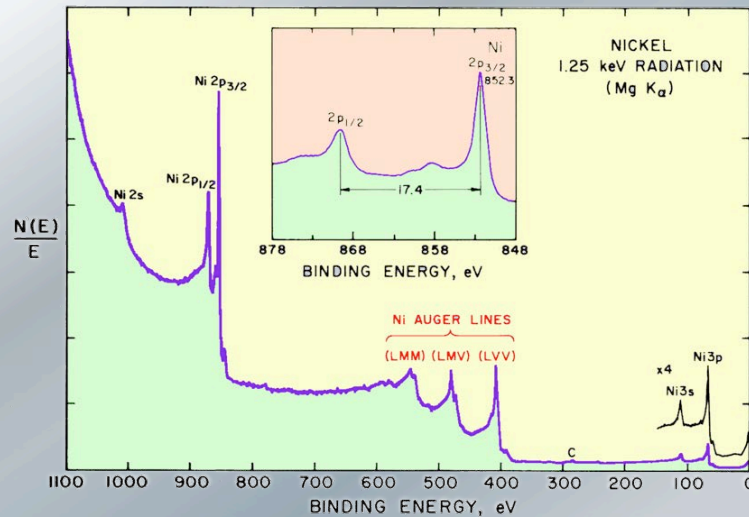- sharp peaks ↔ element-characteristic electron energies

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Spectral Features of XPS

- photoelectron lines

- Auger lines

- shake-up lines

- X-ray satellites

- X-ray ghost lines

- multiplet splitting

- energy loss lines (plasmon lines)

- valence lines and bands

XPS Example: Ni, Irradiated with Mg-K$_\alpha$

NICKEL
1.25 keV RADIATION
(Mg K$_\alpha$)

Ni 2p$_{3/2}$
Ni 2p$_{1/2}$
Ni 2s

Ni
2p$_{3/2}$
852.3

2p$_{1/2}$

17.4

878   868   858   848
BINDING ENERGY, eV

$\frac{N(E)}{E}$

Ni AUGER LINES
(LMM) (LMV) (LVV)

x4
Ni3p
Ni3s
C

1100 1000 900 800 700 600 500 400 300 200 100 0
BINDING ENERGY, eV

XPS Spectra

- photoemission from p, d, and f states with nonzero orbital angular momentum

→ "spin-orbit doublet"

→ 2p$_{1/2}$ and 2p$_{3/2}$ lines (see inset!)

- correspond to final states with

$$j_+ = l + m_s = 3/2; \quad j_+ = l - m_s = 1/2$$

- intensity ratio: $(2j_- + 1)/(2j_+ + 1)$

  → 1:2 for p$_{1/2}$ to p$_{3/2}$

  → 2:3 for d$_{3/2}$ to d$_{5/2}$

  → 3:4 for f$_{5/2}$ to f$_{7/2}$

XPS Spectra

⇒ electrons that escaped without energy loss

- tails at higher energies

  ⇒ electrons that lost energy on escaping from the sample

  ⇒ inelastic scattering

  ⇒ *apparently* higher binding energy

- energy of Mg K$_\alpha$ insufficient to eject K-shell electron from Ni

- but can create vacencies in L and M shells

→ 2s, 2p and 3s, 3p lines

- prominent lines: 2p$_{1/2}$ and 2p$_{3/2}$

XPS Spectra

- after emission of a core electron, for example 2s or 2p: core hole

- can be filled by electron from M shell or the valence band

→ *another* M or V electron carries away the energy

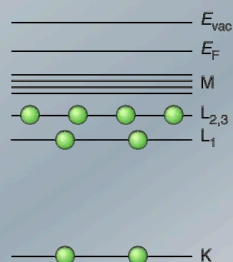→ known as "Auger" process

- dominant up to $Z \approx 35$

→ Auger lines LMM, LMV, LVV in the Ni XPS spectrum

- Auger lines are element-characteristic
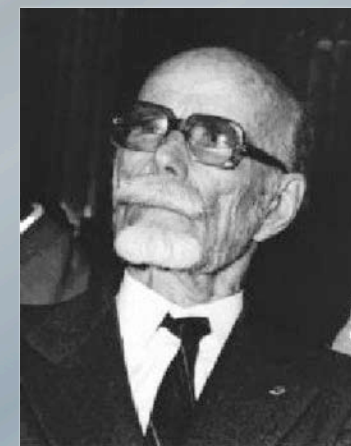
→ can be used for elemental analysis

Principle of AES

- electron or photon in, electron out

- radiation-less transition
  → Auger electron

- electron energy
  ⇒ properties of atom

E_{vac}
E_F
M
$L_{2,3}$
L_1

K

Brief History of Auger Electron Spectrometry

Lise Meitner

Pierre Auger

Brief History of Auger Electron Spectrometry

1923 discovered by Lise Meitner

- reported in Zeitschrift für Physik

- two years before Pierre Auger (?)

- but: English speaking scientific (?) community came to at-tach Auger's name to it

1953 J. J. Lander: idea of using electron-stimulated Auger sig-nals for surface analysis

1967 Larry Harris: demonstrated use of spectrum differentia-tion for enhancing the Auger signals
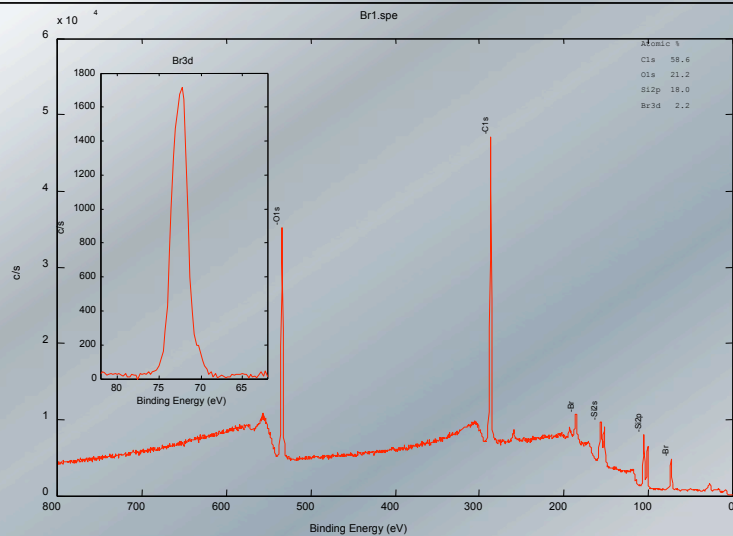
today AES: very frequent analytical method for surfaces, thin-films, and interface compositions

XPS Spectra

- like the photoelectron lines,
  - each Auger line is accompanied by a low-energy tail
  - ↔ energy loss on the outward path

- note that
  - the energy of photoelectrons depends on the energy of the incident photon (linear dependence)
  - the energy of Auger electrons is independent of the in-cident photon energy

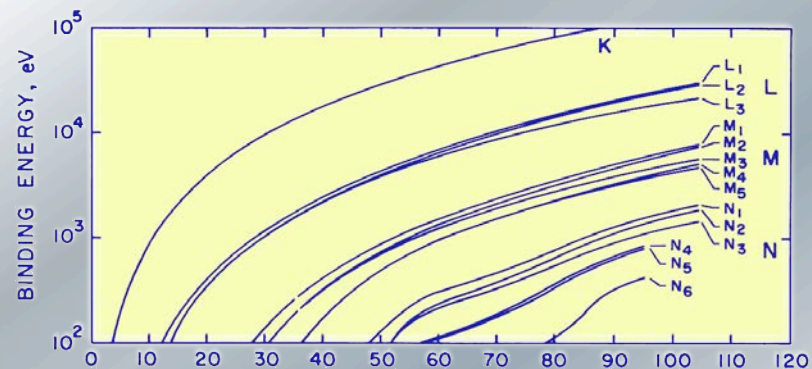# Br-Terminated Self-Assembled Monolayer

Binding Energy and Final-State Effects

- XPS is straight-forward and useful for identification of atomic species at the surface of materials

- neighboring elements in the periodic table can easily be distinguished

- binding energies of adjacent elements for 2s (L1) lines in the third period of the periodic table
  - recorded with Mg K_α (1.25 keV)
  - from early work of Siegbahn

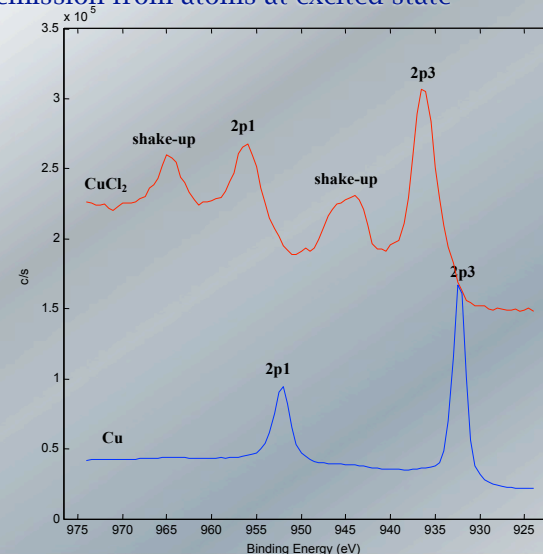# Binding Energies of the Elements

Binding Energy and Final-State Effects

- binding energies increase with the square of the atomic number

- for $Z \geq 30$, photons with energies around $1\,\text{keV}$ can only ionize M or N shell

- recall that binding energy measured in XPS is not equal to bindig energy of an atom in the ground state (with its electron states fully occupied)

    → after ejection of an electron, Coulomb potential of the core is less effectively screened

    → outer shells re-adjust to lower the energy of the final state

    → released energy increases E_{kin} of photoelectron

Shake-up Lines

- emission from atoms at excited state

Binding Energy and Final-State Effects

- readjustment not necessarily to the ground state

→ transitions that produce excited final states

    ○ outer electron may go into excited state

    → "electron shakeup"

    ○ outer electron may go into continuum state "electron shakeoff"

    → less additional energy is given to the photoelectron

    → satellite structure at high binding energy (lower kinetic energy)

Binding-Energy Shifts / Chemical Shifts

- exact binding energy depends on chemical environment of the atom

- consider core level electron

    ○ binding energy ↔ Coulomb interaction

        · other electrons

        · core

    ○ change in chemical environment will re-arrange valence electrons

    ⇒ core level electron will "see" different potential

    ⇒ change in binding energy

Binding-Energy Shifts / Chemical Shifts

- energy of an electron in this level will "see" a different potential
  - → "chemical effect" on the binding energy
  - → "chemical shift"

- example: binding energy of 2p level in Si
  - compare Si-matrix with SiO_2-matrix
  - 2p level shifts by more than $4\,eV$
  - → safe distinction between elemental Si and SiO_2 from XPS spectra

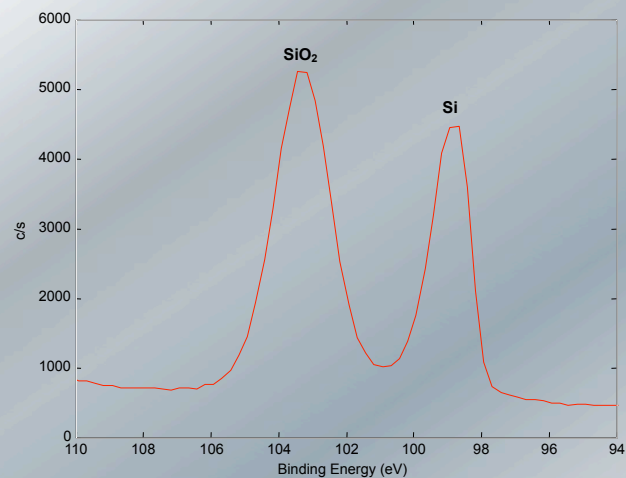- chemical shifts ↔ inner electrons "feel" re-arrangement of valence electrons

Binding-Energy Shifts / Chemical Shifts

- interatomic bonding ↔ electrons drawn from or driven towards the nucleus
- → chemical shifts probe the nature of interatomic bonding
- neighboring atoms with high electro-negativity:
  - withdrawal of electrons, nucleus more "exposed"
  - → increased binding energy
- neighboring atoms with small electro-negativity:
  - addition of electrons
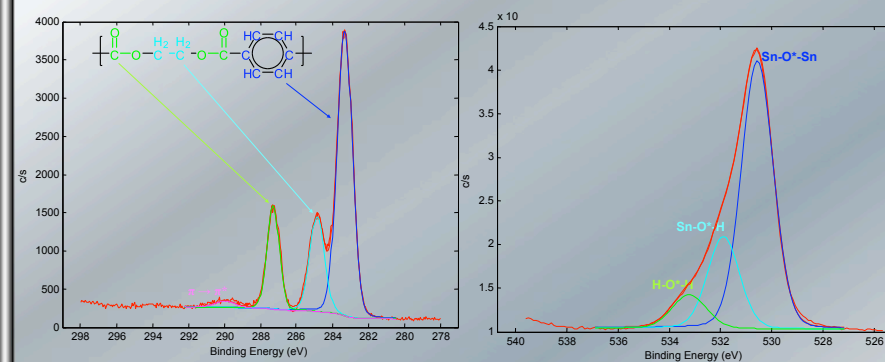 - nucleus less "exposed"
  - → binding energy decreases

Example of Chemical Shift: Si versus SiO_2

Chemical Shift

N₃-Terminated Self-Assembled Monolayer

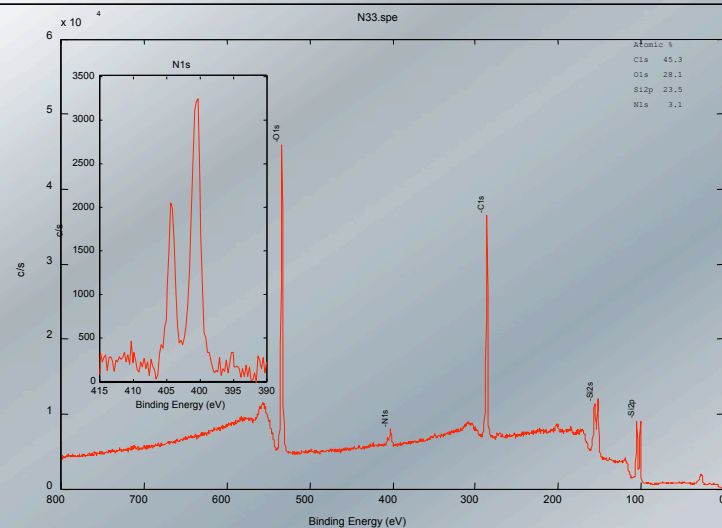N_3-Terminated Self-Assembled Monolayer

N33.spe: Si-C16-N3
2001 Aug 16 Al mono 300.0 W 0.0 45.0° 93.90 eV
Sur1/Full/1
Shyue
4.5834e+004 max   14.67 min
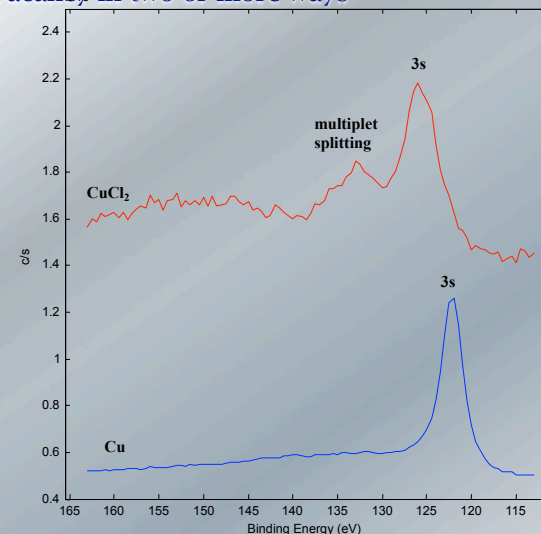
Atomic %
C1s 45.3
O1s 28.1
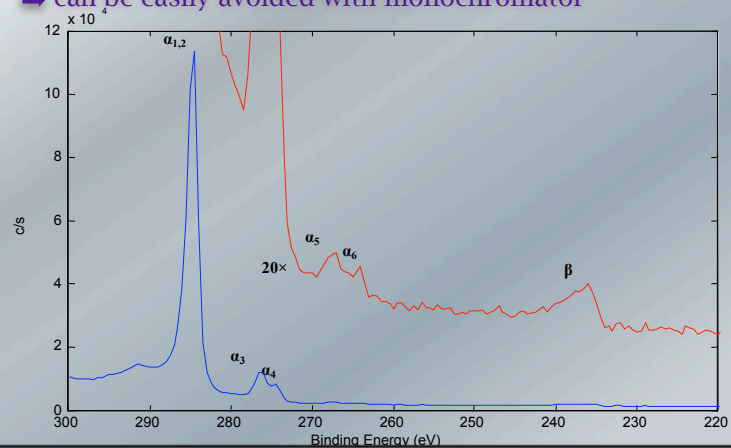Si2p 23.5
N1s 3.1

Multiplet Splitting

- emission from an atom that has a spin can create a vacancy in two or more ways

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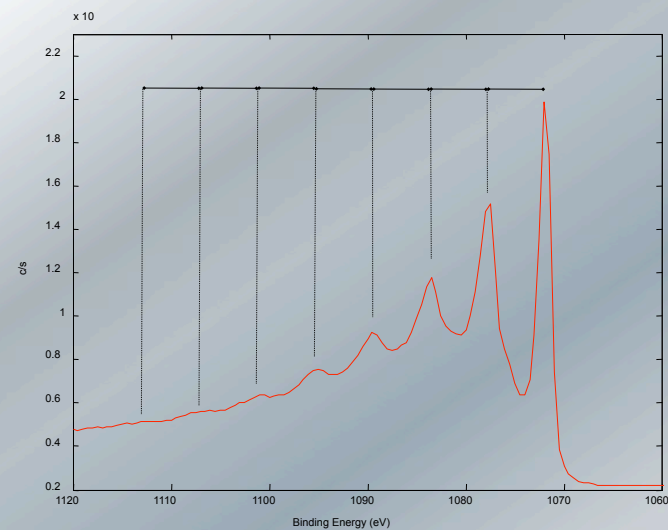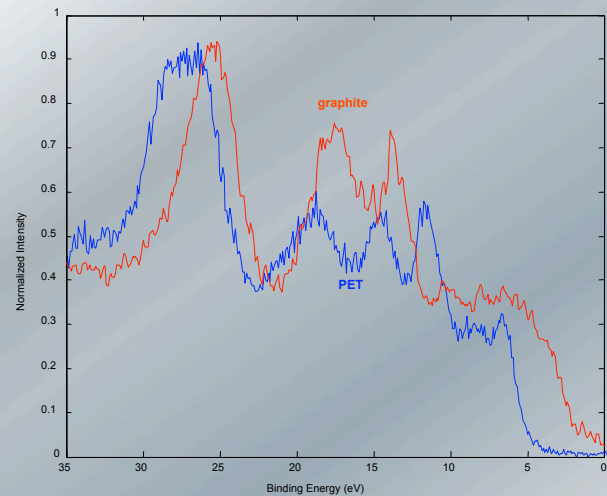## X-ray Satellites and Ghost Lines

- satellites: from X-rays other than Kα1
- ghost lines: from X-rays other than pure anode
- ➡ can be easily avoided with monochromator

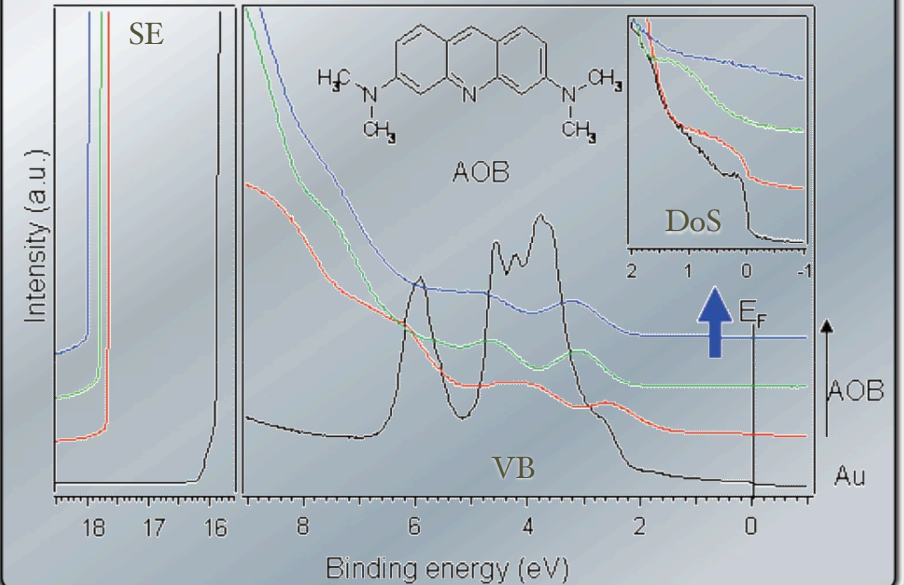

Energy Loss (Plasmon) Lines

Valence Lines and Bands

Example of UPS

Ultraviolet Photoemission Spectroscopy

- ultraviolet photoemission spectroscopy (UPS) generally uses resonant light source, such as a He discharge lamp

- energies in the $16\ldots41$ eV range

- sufficient for analysis of valence-band density-of-states of most solids

- high brightness and small energy widths

- in UPS, different from XPS, the energy resolution is generally limited by the electron energy analyzer, not by the photon source

Work function of Specimen

- Because of the difference in work function of specimen and detector, the kinetic energy measured is different from the true kinetic energy.
  - low energy photoelectron might not reach detector
  - negative sample bias is often used to collect SE
- By definition, work function is the minimal energy required to remove electron from solid
  - the full width of UPS spectra indicate the maximum kinetic energy of photoelectron
  - consider the total energy transfer between photon and electron, the minimal energy required (work function) is (photon energy)-(full width)
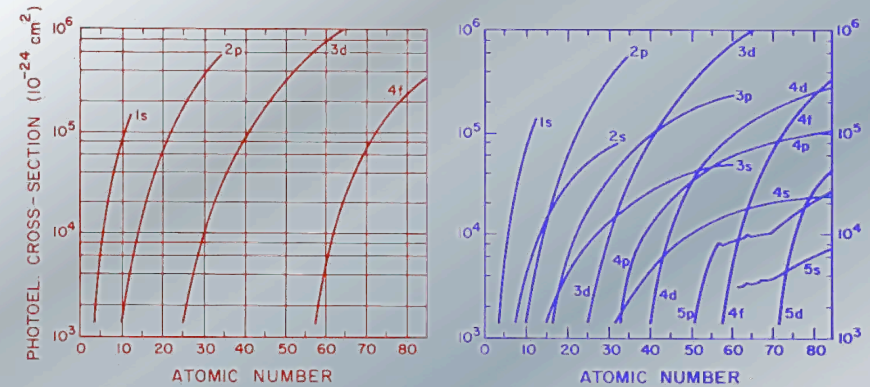
Quantitative Analysis

→ information on composition comes primarily from changes in peak intensity

- line intensities depend on
  - photoelectric cross-section σ
  - electron escape depth λ
  - spectrometer transmission
  - surface roughness
  - presence of a satellite structure
    (→ decrease in main peak intensities)
  - absorption of X-rays is no concern
    (weak compared to electron escape depth)

Photoelectric Cross-Sections

Quantitative Analysis

- line intensities depend on (continued)
  - probability per incident photon for creating a photoelectron in a sub-shell k:

$$P_{\text{pe}} = \sigma^k \cdot N \cdot t$$

  N: atoms per unit volume; t: thickness of the layer from which the electrons escape.

- photoelectric cross-section σ can be measured or calculated

- example of photoelectric cross-sections σ at $1.5\,\text{keV}$
  - for different subshells
  - in units of barns

Quantitative Analysis

→ large variation of photoelectric cross-sections σ!

- comparison with measured cross-sections:
  error of factor ≥ 2 is possible

- number of electrons that can escape from solid without collision decreases with depth x as

$$\text{Exp}\left[-\frac{x}{\lambda}\right]$$

  λ: mean free path length.

→ replace thickness t by mean free path length λ:

$$P_{\text{pe}} = \sigma^k \cdot N \cdot \lambda$$

Quantitative Analysis

- efficiency of producing a peak can vary
  - efficiency typically between 0.7 and 0.8
  - sharp peak in the XPS spectrum will be diminished by influence of excited states (shake-on, shake-off)
  - dependence on chemical environment
- instrumental efficiency T
  - depends on kinetic energy E of the photoelectron
  - usually varies as E^{-1}
  - compare above spectrum: presents $N[E]/E$ rather than $N[E]$

Quantitative Analysis

- further, the photopeak efficiencies are often nearly equal, implying

$$y_A \approx y_B$$

$\rightarrow$ determination of composition ratio from intensity ratio reduces to

$$\frac{n_A}{n_B} = \frac{I_A}{I_B} \cdot \frac{\sigma_B}{\sigma_A}$$

Quantitative Analysis

- chemical analysis often only requires composition *ratio*
  - example: two elements, A and B
  - determination of composition ratio from intensity ratio (peak integral) of XPS lines:

$$\frac{n_A}{n_B} = \frac{I_A}{I_B} \cdot \frac{\sigma_B}{\sigma_A} \cdot \frac{\lambda_B}{\lambda_A} \cdot \frac{y_B}{y_A} \cdot \frac{T_B}{T_A}$$

- often, the photopeaks have about the same energy, implying

$$T_A \approx T_B$$

and
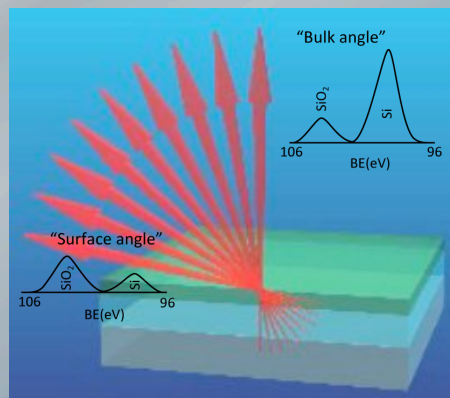
$$\lambda_A \approx \lambda_B$$

General Applications and Advantages of XPS

- mainly chemical binding of atoms in the surface region of a material
- detection of trace elements
  - sensitivity depends on
    - cross-section
    - background from other elements
  - can reach 1 part in 1,000
- XPS is extremely sensitive to surface layers
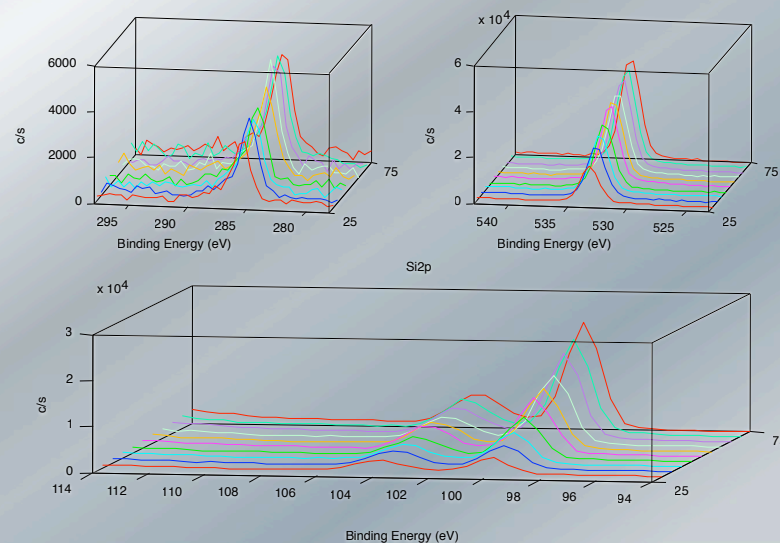- can detect 0.01 monolayers of an element on a surface (!)

Angle-Resolved XPS

- because of the small mean free path
  - signals are from the surface (~nm)
  - the sampling depth is also depends on the take-off angle
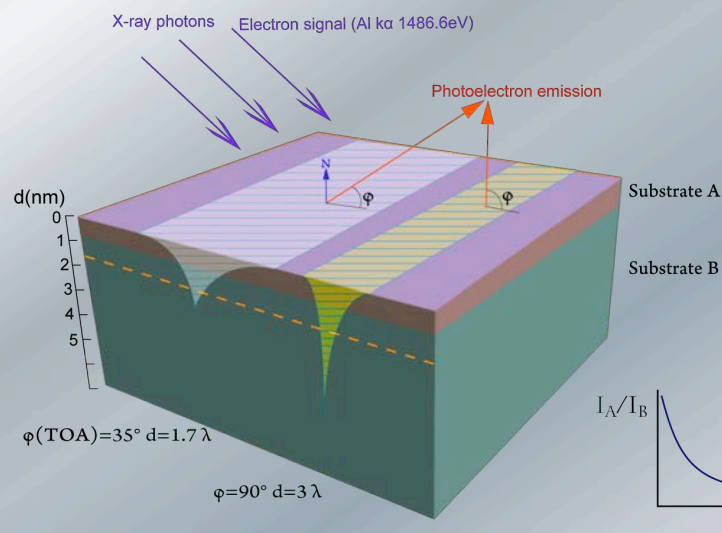 - higher surface-sensitivity with small angle

"Bulk angle"

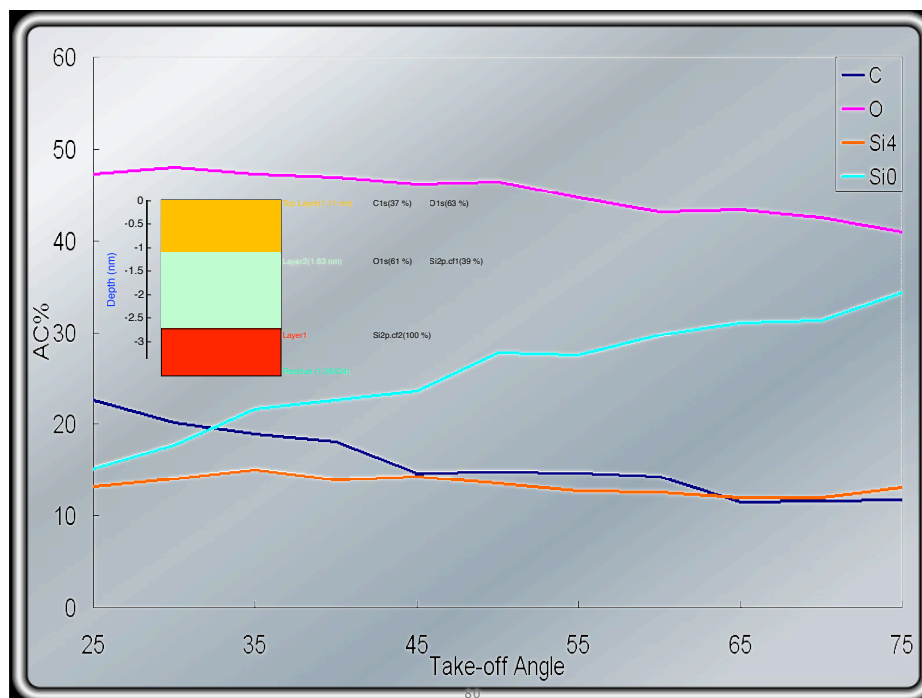SiO₂ Si

106 BE(eV) 96

"Surface angle"

SiO₂ Si

106 BE(eV) 96

Angle-Resolved XPS

c/s 6000 4000 2000 0

295 290 285 280 Binding Energy (eV) 75 25

x 10⁴ 6 4 2 0

540 535 530 525 Binding Energy (eV) 75 25

Si2p

x 10⁴ 3 2 1 0

114 112 110 108 106 104 102 100 98 96 94 Binding Energy (eV) 75 25

c/s

Angle-Resolved XPS

X-ray photons   Electron signal (Al kα 1486.6eV)

Photoelectron emission

N

φ   φ

Substrate A

Substrate B

d(nm)
0
1
2
3
4
5

φ(TOA)=35° d=1.7 λ

φ=90° d=3 λ

I_A/I_B

φ

AC%
60
50
40
30
20
10
0

— C
— O
— Si4
— Si0

Depth (nm)
0
-0.5
-1
-1.5
-2
-2.5
-3

Layer3(1.1 nm)   C1s(37 %)   O1s(63 %)

Layer2(1.63 nm)   O1s(61 %)   Si2p.cf1(39 %)

Layer1   Si2p.cf2(100 %)

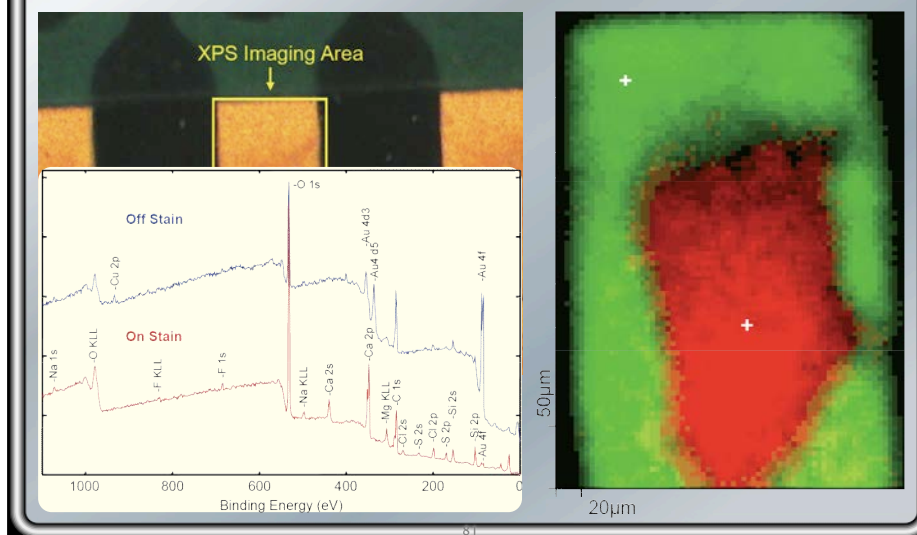Bulk (1.96130)

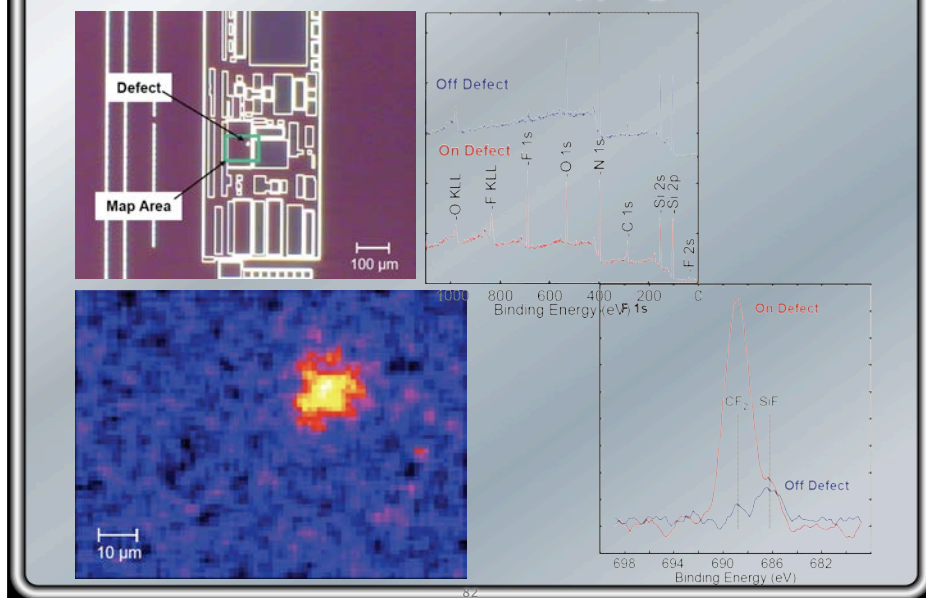25   35   45   55   65   75
Take-off Angle
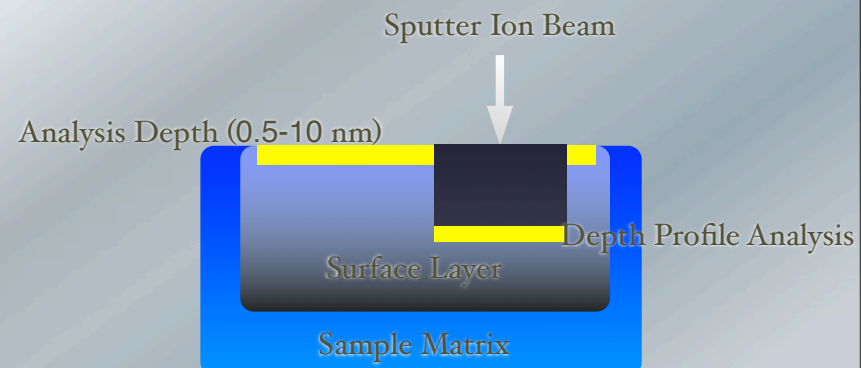
SXM Elemental Mapping

Principle of Depth Profile

- composition depth profiling with *surface* analysis techniques?
- ➡ *erosion* of specimen surface by energetic particle bombardment
- "sputtering"
- two possibilities for analysis:
  - freshly exposed surface (=> XPS, AES)
  - sputtered material (=> SIMS)
- depth profiling -> remove controlled thickness

SXM Elemental Mapping
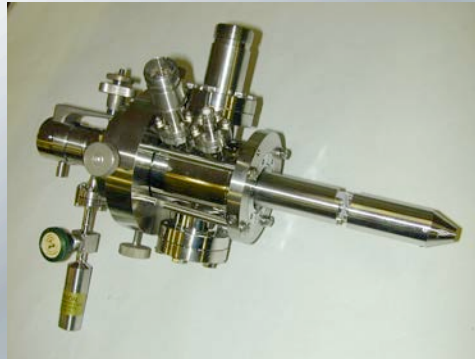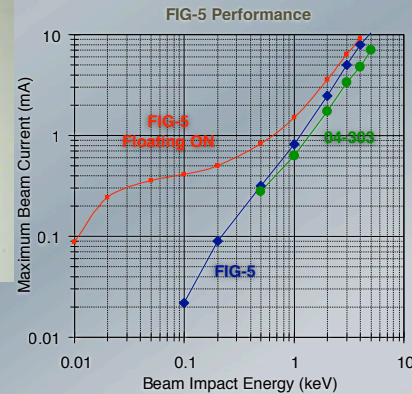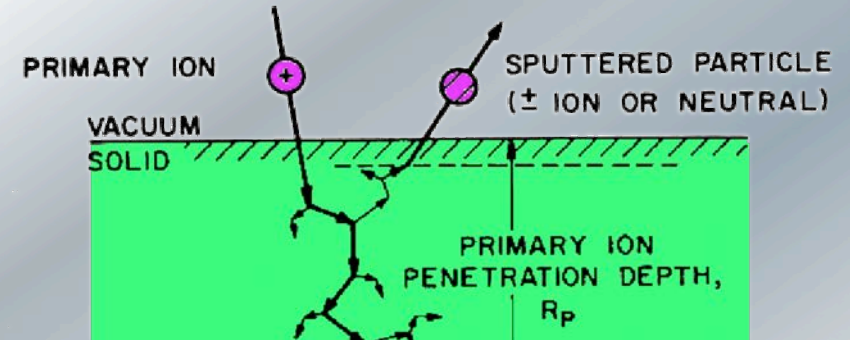

Principle of Depth Profile

Sputter Ion Beam

Analysis Depth (0.5-10 nm)

Depth Profile Analysis

Surface Layer

Sample Matrix

PHI FIG-5 Argon Sputter Ion Gun

- 0-5 kV floating column ion gun
- Settings based software control
- Automatic Ar leak valve

FIG-5 Performance

FIG-5 Floating Column Ion Gun

General Concepts of Sputtering

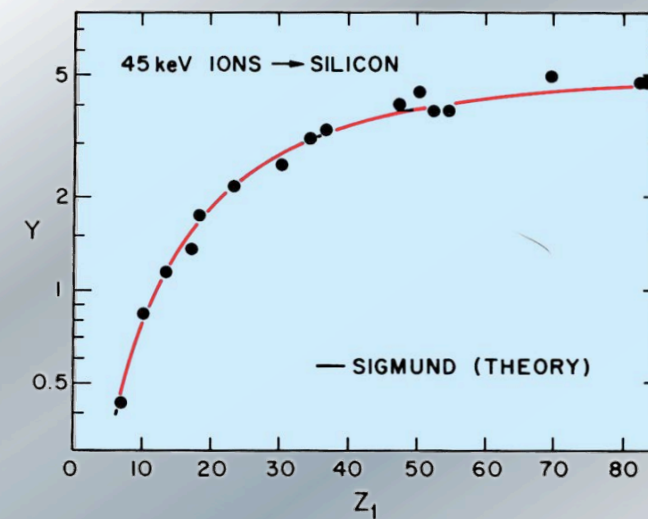## General Concepts of Sputtering

- physical understanding:
  - bombarding ion transfers energy to target atoms
  - these recoil with sufficient energy to generate further recoils
  - some backward-recoiled atoms ($\approx 1..2$ for a $20\,\text{keV}$ Ar^+ ion) approach surface with enough energy to escape
  - these secondary recoils make up most of the sputtering yield
  - the most important parameter in this process is the energy deposited at the surface
  - the sputtering yield should be proportional to number of displaced or recoil atoms

---

Sputtering Yield of Si: Dependence on Incident Ion Mass
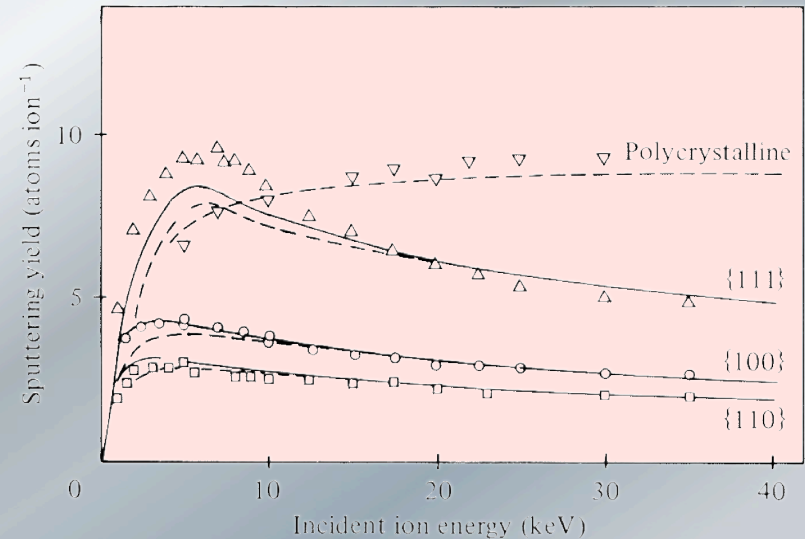
General Concepts of Sputtering

- physical understanding (continued):

  - linear cascade regime (for medium-mass ions as Ar$^+$):

    - number of recoils proportional to the energy deposited per unit depth

    $\Rightarrow$ sputtering yield:

    $$Y = \Lambda \cdot F_D[E_0]$$

    Λ: all material properties (surface binding energies etc.);
    $F_D[E_0]$: density of deposited energy at the surface.

  - $F_D[E_0]$ depends on

    - incident ion (type, energy, direction)
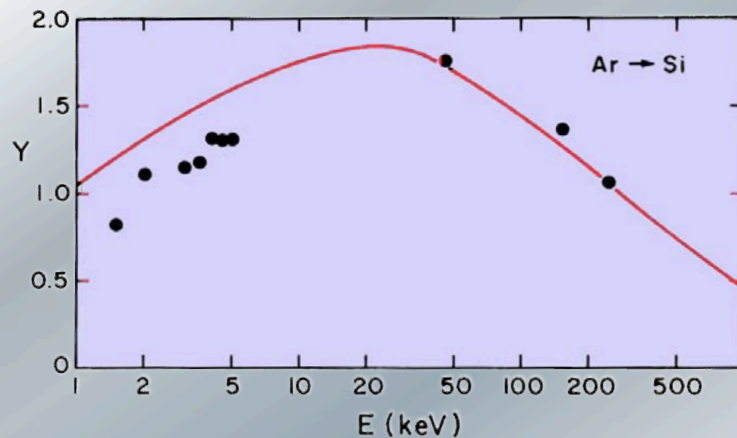   - target parameters (Z_2, M_2, and atomic density N)

Sputtering Yield of Si: Dependence of Incident Direction

Sputtering Yield of Si: Dependence on Ar$^+$ Energy

General Concepts of Sputtering

- deposited energy at the surface can be expressed as

  $$F_D[E_0] = \alpha N S_n[E_0]$$

  $S_{n[E]}$: nuclear stopping cross-section;
  $N \cdot S_n[E]$: nuclear energy loss, $= dE/dx$;
  α: correction factor.

- correction factor α:

  - accounts for
    - angle of incidence
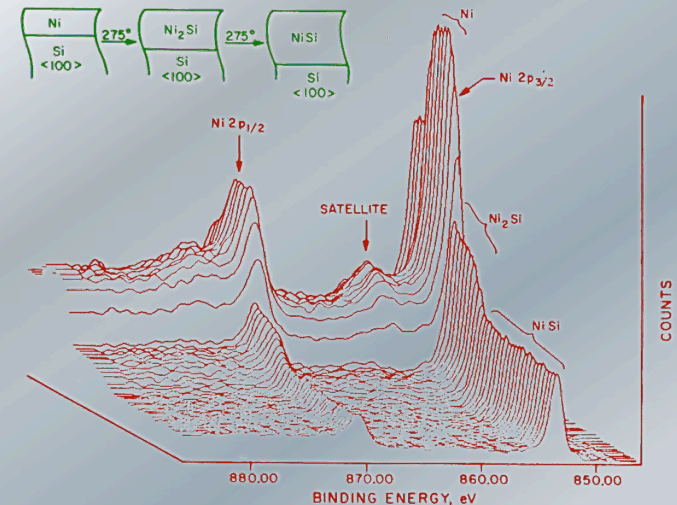   - contributions from large-angle scattering events

General Concepts of Sputtering

- nuclear stopping cross-section $S_n E$:

  - in the keV sputtering regime particle velocity is much less than Bohr velocity

  - → theory must account for screening of nuclear charge by electrons

  - then derive collision cross-section based on screened potential

  - → nuclear stopping cross-section

XPS Example: Formation of Ni Silicides on Tempering Ni Thin-Films on Si

XPS Example: Formation of Ni Silicides on Tempering of Ni Thin-Films on Si

- first stage: formation of Ni_2Si

- second stage: formation of NiSi

- XPS spectra of Ni 2p

- transition from Ni to $NiSi_2$ → shift

- transition from $NiSi_2$ to NiSi → shift

- total transition from Ni to NiSi: shift of $1.1\,eV$

- *decrease in peak intensity*

- → decrease in number density of Ni atoms per cm^2 as compound becomes richer in Si

XPS Depth Profiling

- composition as a function of depth t in thin films

- XPS signal is generated near the surface (~3nm)

- sputtering provides layer sectioning

- depth profiles are usually shown as signal intensity versus sputter time (*not depth*)

- further calibrations required

  - convert sputter time to depth

  - signal intensity to atomic concentration

- however, ion sputtering can causes change in the composition of the surface layers

  - surface segregation

  - preferential sputtering

Preferential Sputtering and Depth Profiles

- potential sputtering artifacts for a multi-component system:
  - preferential sputtering
  - surface segregation

- consider hypothetical system with components A and B
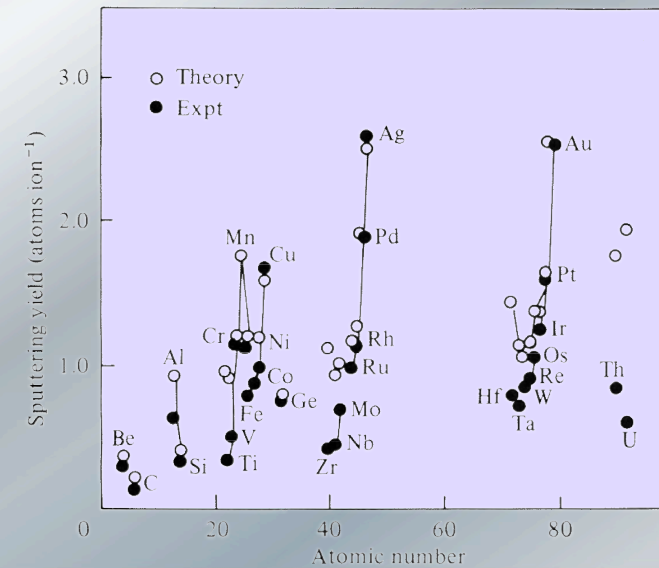
- at the start of sputtering,

$$\frac{C_A^s}{C_B^s} = \frac{C_A^b}{C_B^b}$$

C^s: concentration at the surface;
C^b: concentration in the bulk.

Sputtering Yield: Dependence of Atomic Number

Preferential Sputtering and Depth Profiles

- partial yield of atomic specie A and B:

$$Y_{A,B} = \frac{\text{number of ejected atoms A,B}}{\text{incident particle}}$$

- partial sputtering yield of each element is proportional to its surface concentration C_s

- ratio of partial yields:

$$\frac{Y_A}{Y_B} = f_{A,B} \cdot \frac{C_A^s}{C_B^s}$$

$f_{A,B}$: correction factor.

Preferential Sputtering and Depth Profiles

- $f_{A,B}$ takes into account differences in
  - surface binding energy
  - sputter escape depth
  - energy transfers within the cascade
  - measured values: 0.5..2

→ if $f_{A,B} = 1$, the yield ratio represents the concentration ratio

- if $f_{A,B} \neq 1$, surface concentrations and yields will change from their initial to their final (steady-state) values:

$$C_A^s[0] \quad \rightarrow \quad C_A^s[\infty]$$
$$Y_A^s[0] \quad \rightarrow \quad Y_A^s[\infty]$$

Preferential Sputtering and Depth Profiles

- at $t = 0$,

$$\frac{Y_A[0]}{Y_B[0]} = f_{A,B} \cdot \frac{C_A^s[0]}{C_B^s[0]} \equiv f_{A,B} \cdot \frac{C_A^s}{C_B^s}$$

- after long time, when steady state is reached, the conservation of mass requires that the ratio of partial yields corresponds to the bulk concentration ratio:

$$\frac{Y_A[\infty]}{Y_B[\infty]} = \frac{C_A^b}{C_B^b}$$

- now consider the case of

$$f_{A,B} > 1$$

↔ A sputters faster than B

Preferential Sputtering and Depth Profiles

→ the surface concentration ratio *rearranges*

- eventually produces sputtering yields representing the *bulk* concentration ratio

- example of the compositional change at the surface:
  - sputtering of PtSi
  - 20 keV Ar$^+$
  - analyzed by RBS with 2 MeV ^{4}He ions
  - spectrum shows enrichment of Pt at the surface (shaded)

Preferential Sputtering and Depth Profiles
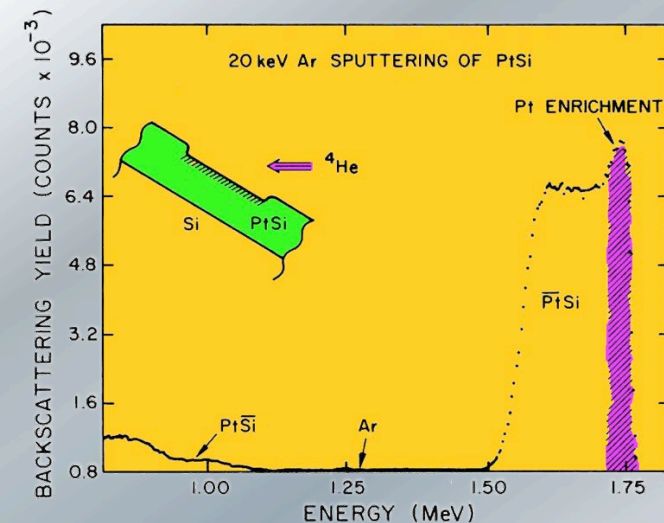
⇒ enrichment of B at the surface

⇒ Y_B increases, while Y_A decreases

- as time progresses, the enrichment of B approaches the level at which
  - the increased concentration of B balances the preferential sputtering of A
  - a steady state is reached
  - the ratio of surface concentrations deviates from the ratio of bulk concentrations if $f_{A,B} \neq 1$

$$\frac{C_A^s[\infty]}{C_B^s[\infty]} = \frac{1}{f_{A,B}} \cdot \frac{C_A^b}{C_B^b}$$

Example: PtSi

Preferential Sputtering and Depth Profiles

⇐ preferential Si sputtering

• dose dependence of partial sputtering yields of Si and Pt:

→ in the beginning, the sputtering yield of Si is 2.4 times larger than that of Pt

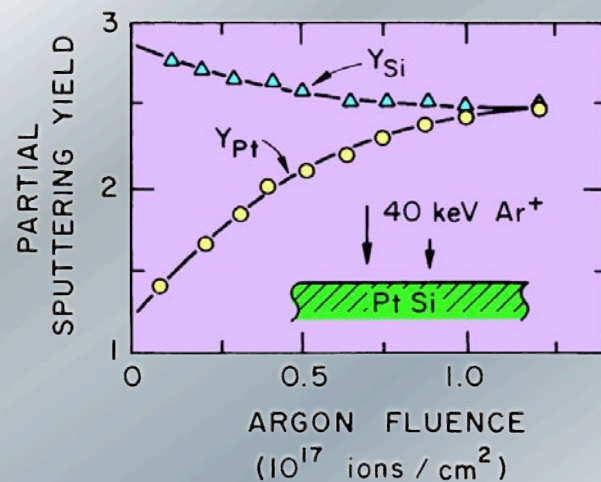• asymptotic approach to steady state, where $Y_{Si} = Y_{Pt}$

Interface Broadening and Ion Mixing

• important application of SIMS:
  analyze composition of buried interfaces in layered thin film systems

• however, penetration of sputter beam ions can cause inter-mixing at buried interfaces

⇒ artificial broadening of concentration profile across the interface

• example:
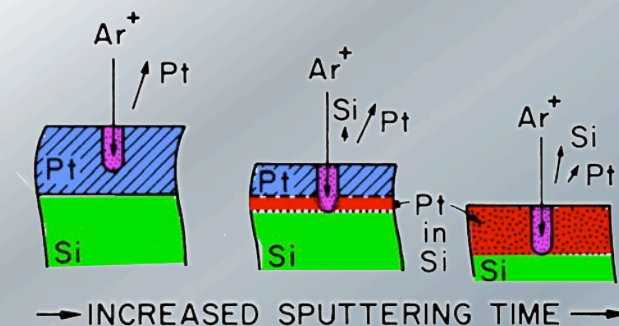 Ar^+ sputtering of a $100\,nm$ thick Pt layer on Si

Example of Dose Dependence of Partial Sputtering Yield

Example: Pt layer on Si

• sputtering process after three different times
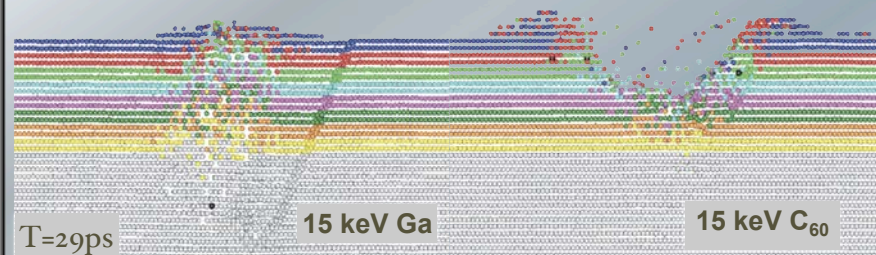
• additional aspect: shape of the crater

Interface Broadening and Ion Mixing

⇒ Si signal will appear before Pt layer is sputtered away completely

⇒ Pt signal will still be present shortly after the sputtered depth has reached the thickness of the Pt layer

- interfacial broadening corresponds to twice the range R of the sputtering ion

- amount of interface broadening can be minimized by proper choice of energies and incident angles

- artifacts can be eliminated by complementary technique

C_{60} bombardment calculations, Zbigniew Postawa; Enhancement of Sputtering Yields due to C_{60} vs. Ga Bombardment of Ag{111} as Explored by Molecular Dynamics Simulations, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, Anal. Chem.y, 75, 4402-4407 (2003); Microscopic insights into the sputtering of Ag{111} induced by C_{60} and Ga Bombardment,[*ibid.*, J. Phys. Chem., submitted January 2004
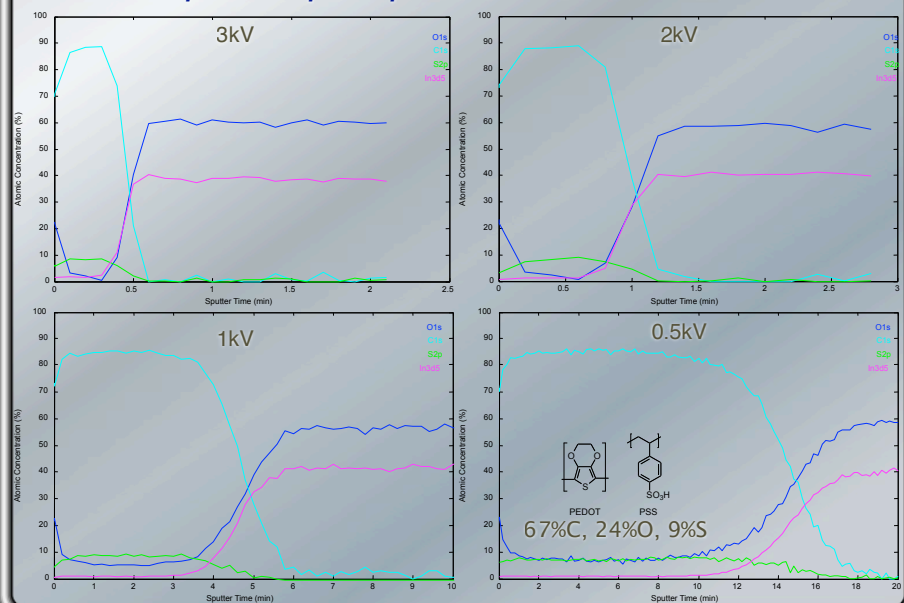

Sputtering with C60 Ions

- **Traditional ion sources such as Ar and Ga can impart significant damage to a samples surface**
- **C60 ions are more efficient in removing material and leave behind a relatively thin damage layer**

T=29ps   15 keV Ga   15 keV C_{60}

Depth Profile of PEDOT:PSS on ITO: Ar

PEDOT   PSS
67%C, 24%O, 9%S

Requisites for Molecular Depth Profiling

Condition for molecular depth profiling…
⇒ damage must be removed as fast, or faster, than created
∴ sputtered depth > range

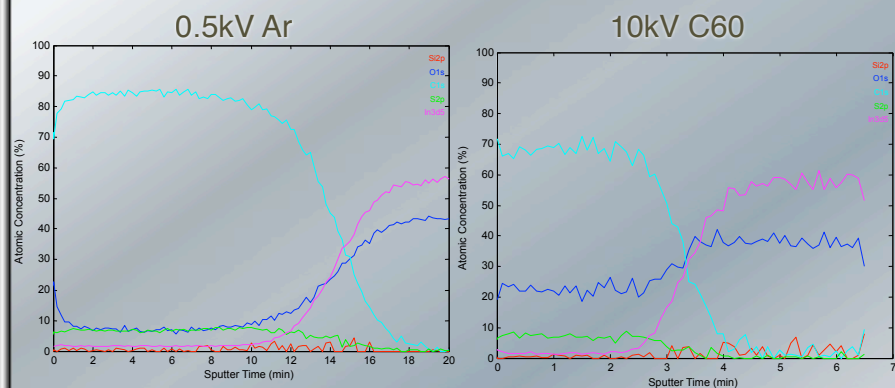| 10 keV	rel. yield (Ga=1)‡	σ_d (cm²)	range (nm)*	removed depth (nm)**
SF_5	100	5x10⁻¹³	9.8	0.06
Au_3	1,000	1x10⁻¹²	19	0.3
C_{60}	2,000	2x10⁻¹³	2.6	3.3
Au_{400}	20,000	†2x10⁻¹³	6.6	3.4

‡Adapted from Kersting, et al. *Appl. Surf. Sci.* (2004) and Tempez, et al. *Rapid Comm. Mass Spectr.* (2004).
†Conservatively estimated lower limit. Values of σ_d are applicable to most organic systems.
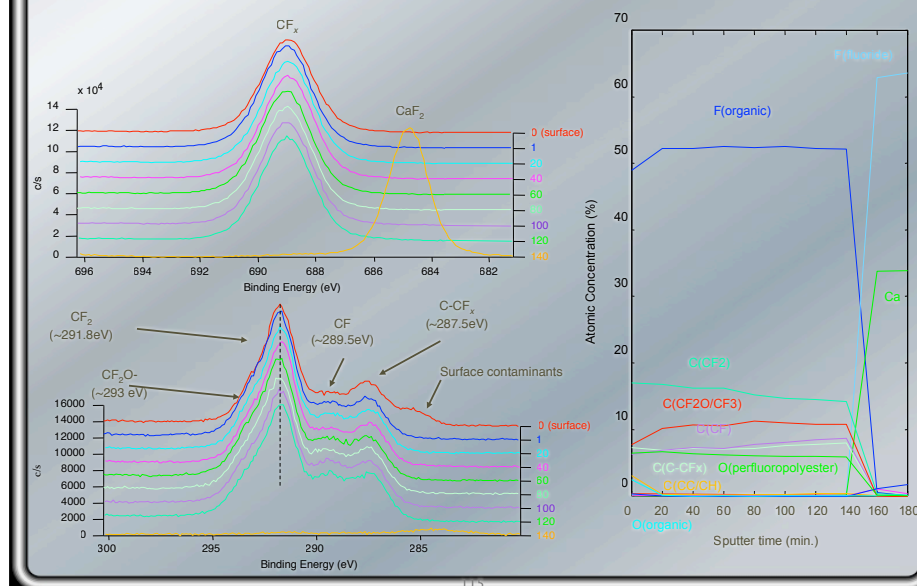*Calculated using SRIM2003.
**Calculated using relative yield and σ_d, in good agreement with Delcorte, et al. *NIMB* (2000) and Postawa, et al. *J. Phys. Chem. B* (2004).

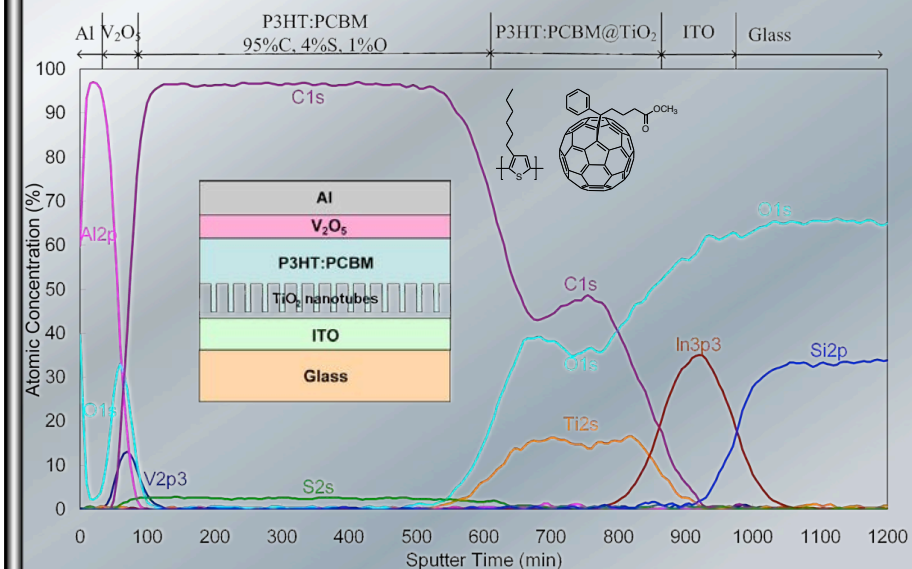# PEDOT:PSS on ITO Glass

0.5kV Ar

10kV C60
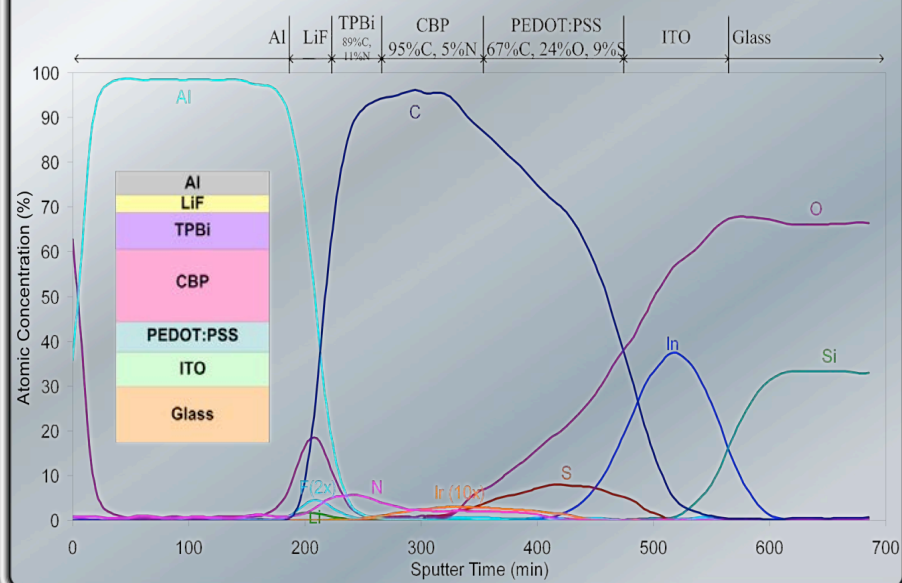

Perfluoropolyester on CaF₂

Why Use C60 Ion Sputtering for XPS

- XPS is widely used to study the surface chemistry of polymer and organic materials

- To probe below the surface argon (Ar) ion sputtering is typically used to remove material

- It is generally not possible to apply this approach to polymers or organic materials because of the high level of chemical damage caused in the surface region by the argon ions

- C_{60} ion sputtering has been demonstrated to be effective for sputter etching many polymer and organic materials while causing minimal chemical damage to the sample surface
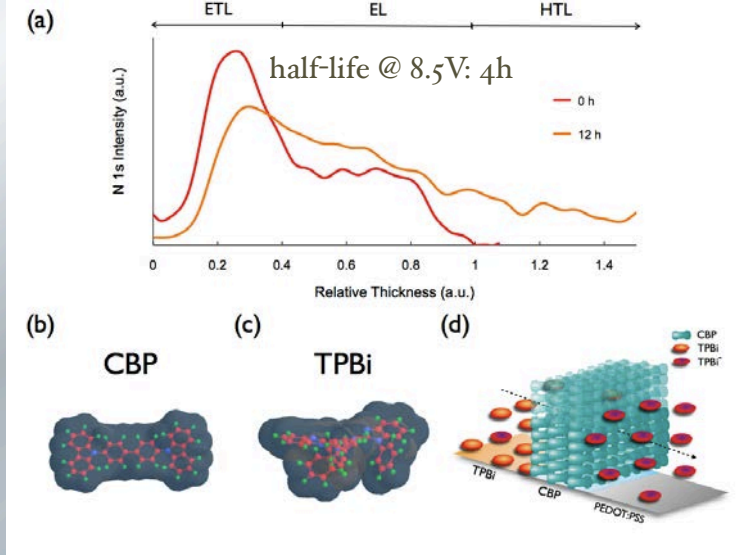
Depth Profile of a Solar-Cell

Depth Profile of Complete OLED Device

Retarding Migration of Molecules

half-life @ 8.5V: 4h

(a) ETL | EL | HTL

(b) CBP (c) TPBi (d)

Device after Aged at 5V DC for 12 h