



Chemical Surface Analysis and Plasma Treatment

Andreas Dahlin
Lecture: 6/7

adahlin@chalmers.se
<http://www.adahlin.com/>

2024-02-05

Surface Engineering

1



Outline

We have looked at techniques that detect if something binds to a surface. (SPR, QCM etc.)

Now we will look at methods to identify what is on a surface (or what the surface of a material consists of).

We will also do a brief overview of plasma techniques for modifying surfaces.

2024-02-05

Surface Engineering

2



General Considerations

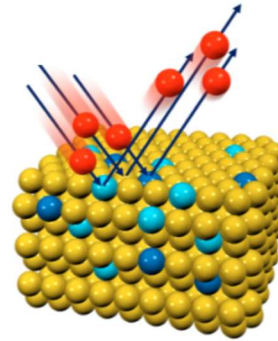
The general idea of chemical surface analysis is to send “something” onto the surface and look at “what comes out”.

We can basically send in ions, electrons or photons. They can have different energies (wavelengths).

Probing depth is generally highest for photons, while ions do not penetrate far into the material.

We can measure the kinetic energy or mass of the ejected particles (ions or electrons).

Alternatively, we look at photons reflected from the surface.



2024-02-05

Surface Engineering

3



X-ray Photoelectron Spectroscopy

Most established technique for chemical analysis. Also called electron spectroscopy for chemical analysis (ESCA).

Essentially based on the photoelectric effect discovered by Einstein.

Detects all elements (except H and He).

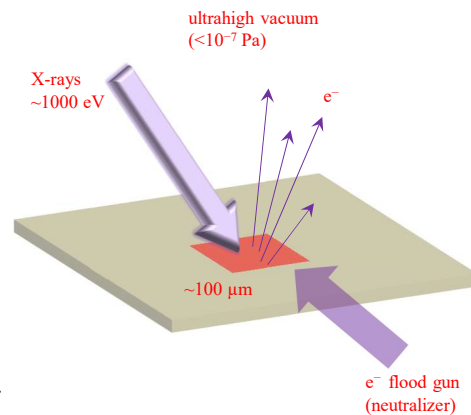
Send in x-rays with known energy W_{ray}

Measure kinetic energy W_{kin} of ejected electrons.

The missing energy is that of the chemical bond:

$$W_{\text{bond}} = W_{\text{ray}} - W_{\text{kin}}$$

The result is a *spectrum* showing the dispersion of electron energies.



2024-02-05

Surface Engineering

4

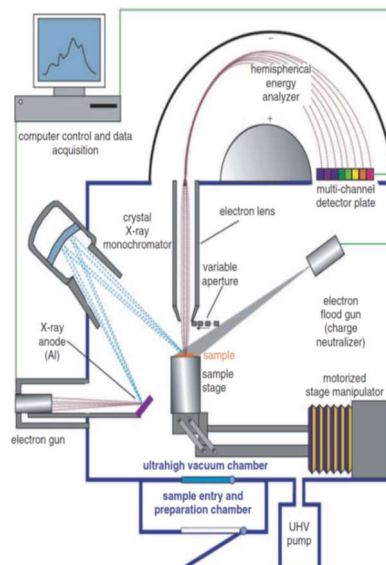


Instrument

Summary of components:

- Vacuum pump
- X-ray source
- Electron energy analyzer
- Electron flood gun (sometimes also Ar^+)
- Sample handling

Not pocket sized!



2024-02-05

Surface Engineering

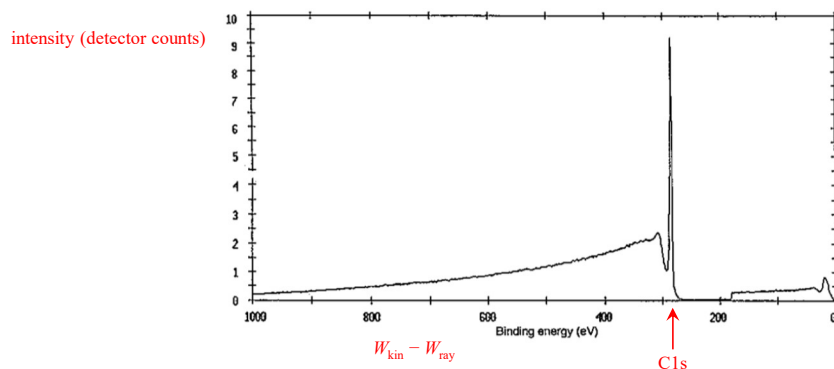
5



Example Spectrum

Simplest possible spectrum: polyethylene ($-\text{CH}_2-\text{CH}_2-$)

C1s peak is always present due to unavoidable contaminations. Use for calibration of energy axis!



2024-02-05

Surface Engineering

6



Quantification

Photoelectron generation probability generally increases with atomic number but varies with electron orbitals.

Absolute quantification (mass per area) is very difficult, but relative quantification (fractions) of the different elements is very accurate!

Known *sensitivity factors* are used to normalize the signals (area under peaks). They represent the probability of electron emission for different elements and orbitals.

Detection limit generally 0.1-1% (atom fraction).

Binding energy (referred to C1s at 285.0eV)	Element and line identification	Peak area (counts)	Sensitivity factor	Normalized peak area	Atomic %
285.0	C 1s	27,45	0,314	87,423	32,1
685.6	F 1s	124,04	1,000	124,04	45,5
131.8	P 2p	9,53	0,525	18,158	6,7
395.0	N 1s	7,15	0,499	14,338	5,2
531.0	O 1s	21,08	0,733	28,761	10,5

definition of unity →

2024-02-05

Surface Engineering

7

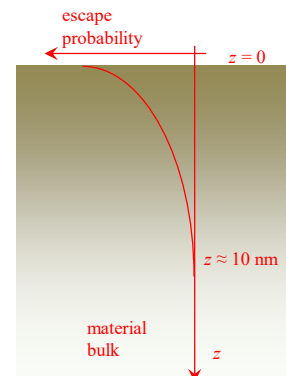


Probing Depth

The photoelectrons come from the top ~10 nm in the material.

Note that the x-rays can go deep into the material! However, photoelectrons coming from the material bulk are very unlikely to reach the surface and escape. (They undergo collisions, recombination etc.)

The weighting function is exponential with depth.



2024-02-05

Surface Engineering

8

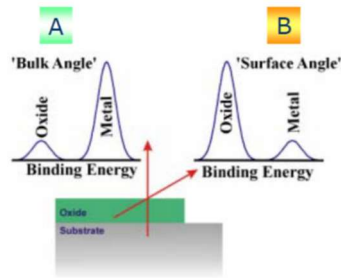


Depth Probing

By tilting the sample relative to the detector (not the source), the probing depth changes to a lower value.

It is not possible to probe deeper than the *mean free path* of the electrons in the material.

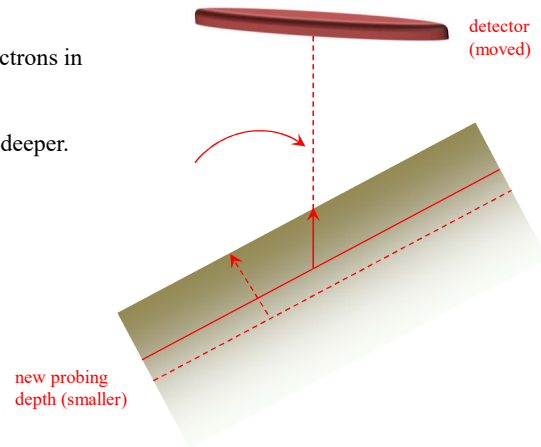
However, XPS can be combined with ion beam etching to analyze deeper.



2024-02-05

Surface Engineering

9

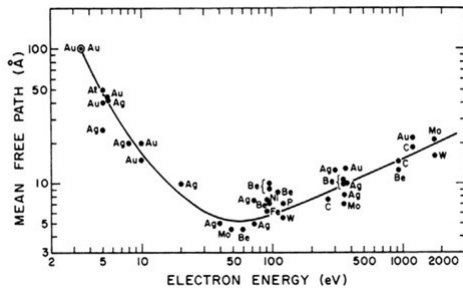


Alternative Depth Probing

An alternative is to use several different x-ray energies, though it not so easy to change this parameter.

The photon energy influences the electron energy and thus its mean free path in the material. If the mean free path is higher the probing depth increases.

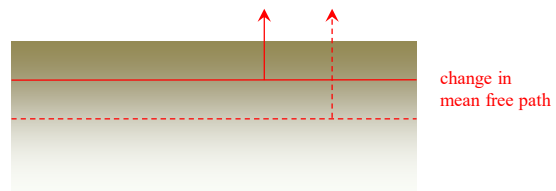
The mean free path is almost universal with photon energy, but the dependence is not monotonic!



2024-02-05

Surface Engineering

10



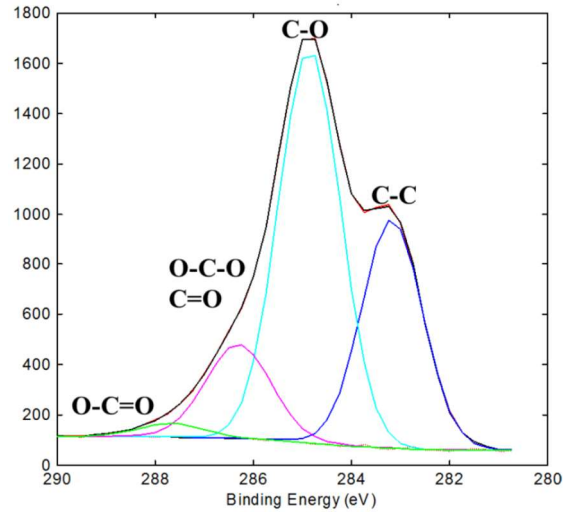


Bond Analysis

The exact electron energy depends on the chemical bond.
High resolution spectra can reveal such information.

Peaks are often overlapping and analysis requires fitting multiple peak functions (e.g. Gaussian).

Often used to analyze the carbon region in the spectrum.



2024-02-05

Surface Engineering

11



XPS Pros and Cons

- ☹️ High vacuum required.
- ☹️ No absolute quantification of mass coverage.
- ☹️ Reasonable detection limit.
- ☹️ Not terribly destructive (x-ray bombardment).
- 😊 Accurate relative quantification of elements.
- 😊 Identification of chemical bonds.

2024-02-05

Surface Engineering

12



Energy Dispersive X-ray (EDX) Analysis

An additional feature in electron microscopy.

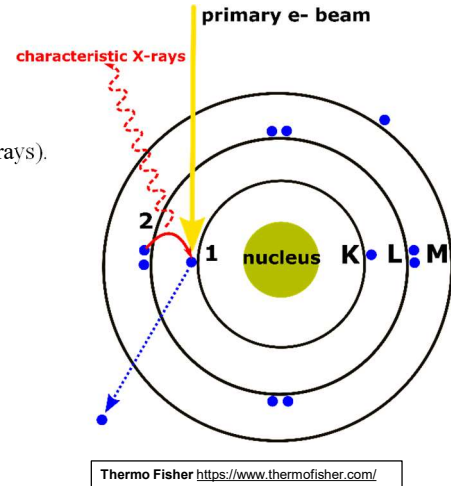
Note main difference compared to XPS: electrons in, photons out!

Like XPS, not very destructive (electron beam bombardment instead of x-rays).

Much higher resolution than XPS due to precise beam focus.

Same kind of quantification of elements, accurate but relative.

Hard to use with organic compounds!



2024-02-05

Surface Engineering

13



Mass Spectrometry

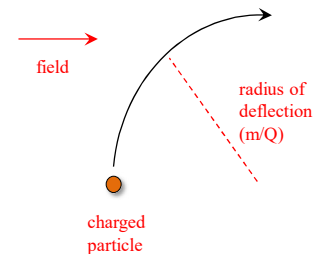
Several techniques exist, the common principle is to analyze mass of molecules or fragments of molecules.

Secondary ion mass spectroscopy (SIMS) is commonly used for surface analysis.

Spectrum of intensity vs *mass to charge ratio* (m/Q).

Generally the best detection limits (ppm or even ppb).

It is assumed that all ions are accelerated to the same kinetic energy before going to the detector.



2024-02-05

Surface Engineering

14



The Sputtering Process

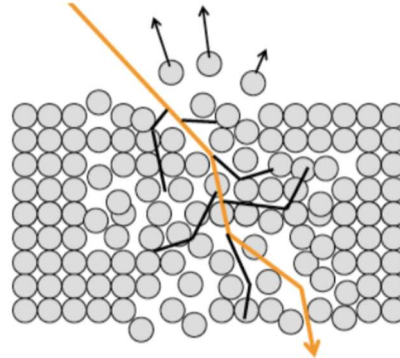
The primary ions (e.g. Ga^+) hit the surface with high energy.

The focused beam is a few nm in diameter.

The sample is damaged (milled) and primary ions are even implanted in the material.

It is easy to generate fragments from ion bombardment, typically 1-10 per primary ion, but they must be charged to have a chance to be detected.

The yield of secondary ions is much lower (from one down to 10^{-6}) and very hard to know. As a result, quantitative analysis is difficult!



2024-02-05

Surface Engineering

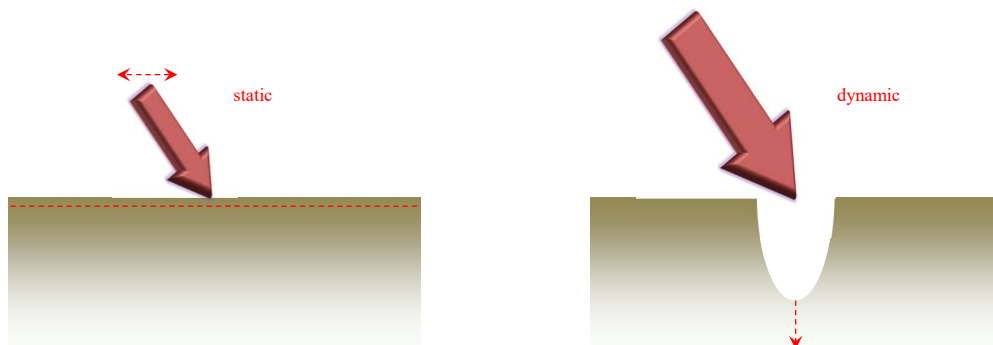
15



Static and Dynamic SIMS

Static mode: The ion dose is low enough to not mill the sample when scanned over a large area. All secondary ions will originate from the top ~3 atomic layers.

Dynamic mode: The ions keep milling the sample at the same location with high beam intensity. Ion fragments are continuously being generated but come from deeper inside the sample as time progresses.



2024-02-05

Surface Engineering

16



Time of Flight Analyzer

The finest resolution is given by measuring the *time of flight* of the ions travelling a certain distance.

Requires a pulsed ionization.

All ions are accelerated to the same kinetic energy by a certain voltage, but their velocity will differ (and thus time of flight).

High detection yield because it does not filter out only some fragments.

Higher resolution in the spectrum.

Suitable for static SIMS, not dynamic!

2024-02-05

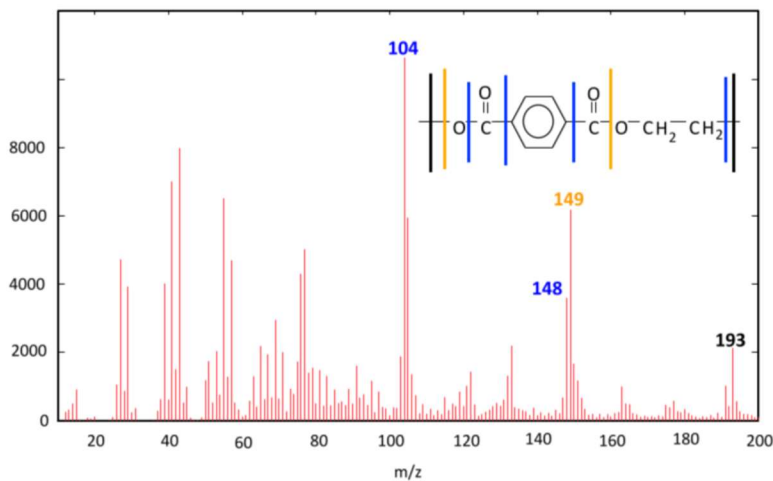
Surface Engineering

17



Example Spectrum

Fragments of poly(ethylene terephthalate).



2024-02-05

Surface Engineering

18



Matrix-Assisted Laser Desorption Ionization

Matrix-Assisted Laser Desorption Ionization (MALDI) is another method of ionization (not detection) that minimizes fragmentation.

The molecular weight of large molecules can be measured.

Very useful for polymers and proteins!

Not a surface analysis method. Special sample preparation needed. However, very small amounts ($\sim 1 \mu\text{g}$) are required so you might actually get enough from a surface if it is large!

Another ionization method with little fragmentation is electrospray ionization, but this requires more material because the ionization is run continuously, while MALDI uses pulses.

TOF detectors are often used with MALDI because of their wide mass range.



Ion Scattering Spectroscopy

A beam of ions (typically He^+ or Ar^+) is directed at the surface.

The energy of ions scattered from the surface is measured. It will depend on what surface atoms they have bounced into, primarily their mass.

ISS is extremely “surface sensitive”, with only the top-most atomic layer being probed. Hence the sensitivity to surface contaminations is also extreme.



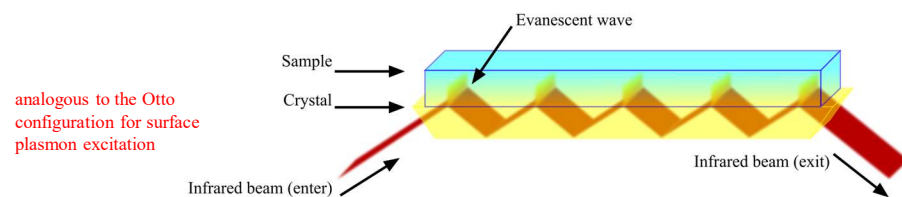
Infrared Spectroscopy

Just like ordinary vibrational spectroscopy, but the attenuated total reflection (ATR) mode makes the technique surface sensitive. The sample is in direct contact with a crystal where light is confined.

Multiple reflections for higher signal.

Penetration depth into sample relatively large (compared to XPS and mass spectroscopy).

Detection limit not as high as in XPS and SIMS but very simple to do and no vacuum needed!



Wikipedia: Attenuated total reflectance

2024-02-05

Surface Engineering

21

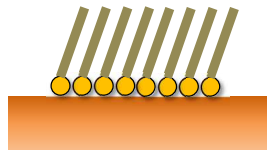


Are All Modes Excited?

If the molecules have a certain orientation, it is not certain that all modes can be excited.

First, the dipole of the vibration mode must not be parallel to the propagation of the incident light.

On metal surfaces, the dipole of the vibration mode must not be parallel to the surface (surface dipole selection rule).



2024-02-05

Surface Engineering

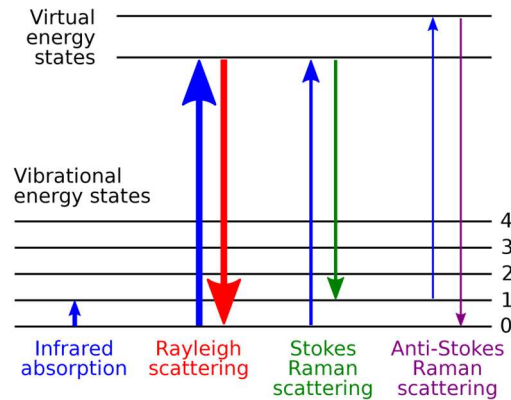
22



Raman

Raman spectroscopy is similar and complementary to FTIR, but based on *inelastic scattering* of photons.

- Imaging of samples! Collect spectra from different spots.
- Higher spectral resolution than FTIR.
- More frequencies accessible.
- Can measure in water.
- Some modes are only active in Raman, not FTIR.



Wikipedia: Raman spectroscopy

2024-02-05

Surface Engineering

23



Plasma

Known as “the fourth state” of matter, but there are no defined phase transitions to or from a plasma state.

A plasma contains many charged particles, ions or electrons. It is extremely conductive!

It is created by subjecting a gas to a strong electric field and/or heat.

Many gases can be used: O₂, Ar, CF₄, N₂ etc.



CDON <http://www.cdon.se>

2024-02-05

Surface Engineering

24

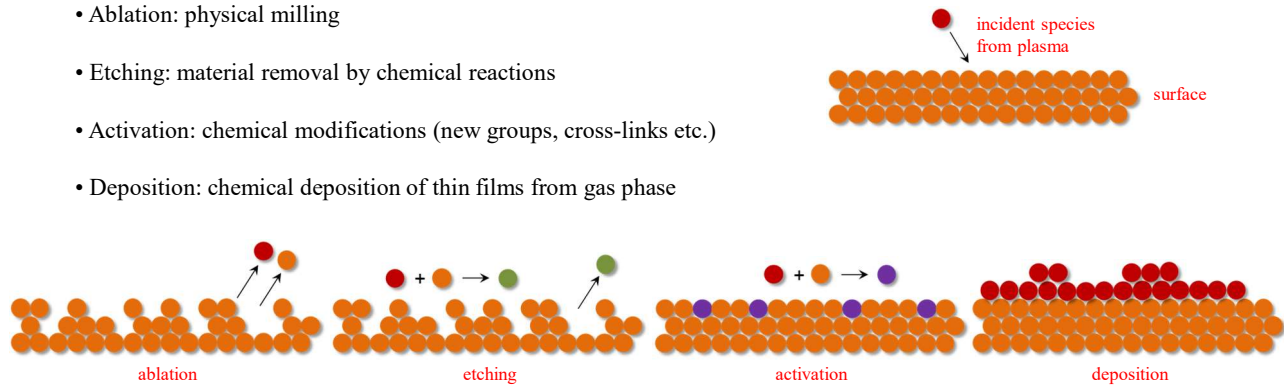


Plasma Treatments

Plasma treatments are simple to do, but it is very difficult to know what happens on the surface.

One can distinguish between different processes:

- Ablation: physical milling
- Etching: material removal by chemical reactions
- Activation: chemical modifications (new groups, cross-links etc.)
- Deposition: chemical deposition of thin films from gas phase



2024-02-05

Surface Engineering

25



Atmospheric Plasma

Compressed air delivered through a nozzle with a high electric potential applied (not heating) which ionizes the gas.

No need for vacuum!

Harder to modify surfaces on the interior of objects because the nozzle cannot access.

Often used to improve adhesion and/or wetting of paint on low surface energy materials. The effect wears off though if the paint is not applied!



Princeton Scientific <https://princetonscientific.com/>

2024-02-05

Surface Engineering

26



Videos: Plasma

- Plasma treatment of plastics (ancient and cool video)
- Bottle barriers
- Making hydrophobic coatings

2024-02-05

Surface Engineering

27



Checklist 6

- XPS instrument design
- Sensitivity factors and quantification
- Static and dynamic SIMS
- TOF detectors
- Principles of IR and Raman
- How plasma can modify surfaces

2024-02-05

Surface Engineering

28



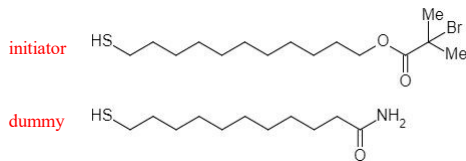
Exercise 6.1

You are modifying gold surface with initiators for polymerization reactions.

How can you determine that the initiator is bound? Discuss which technique would be most simple.

You suspect the Br group might spontaneously leave the surface. How could you check if this is the case?

You want to control the amount of initiators on the surface by mixing it with a “dummy” that has no Br groups. How can you determine the ratio of initiator to dummy groups on the surface?



2024-02-05

Surface Engineering

29



Exercise 6.2

In static SIMS, Ga^+ ions hit the surface of a silicon wafer. An area of $100 \times 100 \mu\text{m}^2$ is analyzed with a current of 1 pA. Si atoms have a size of 420 pm. How long can the exposure time be in total to cause insignificant damage, meaning that maximum 10% of the top layer of atoms is destroyed? Assume a sputter yield of one, i.e. each ion hits one atom. How many secondary ions are generated if the yield is 10^{-3} ?

→

908 s, ~6000 ions are generated per second

2024-02-05

Surface Engineering

30