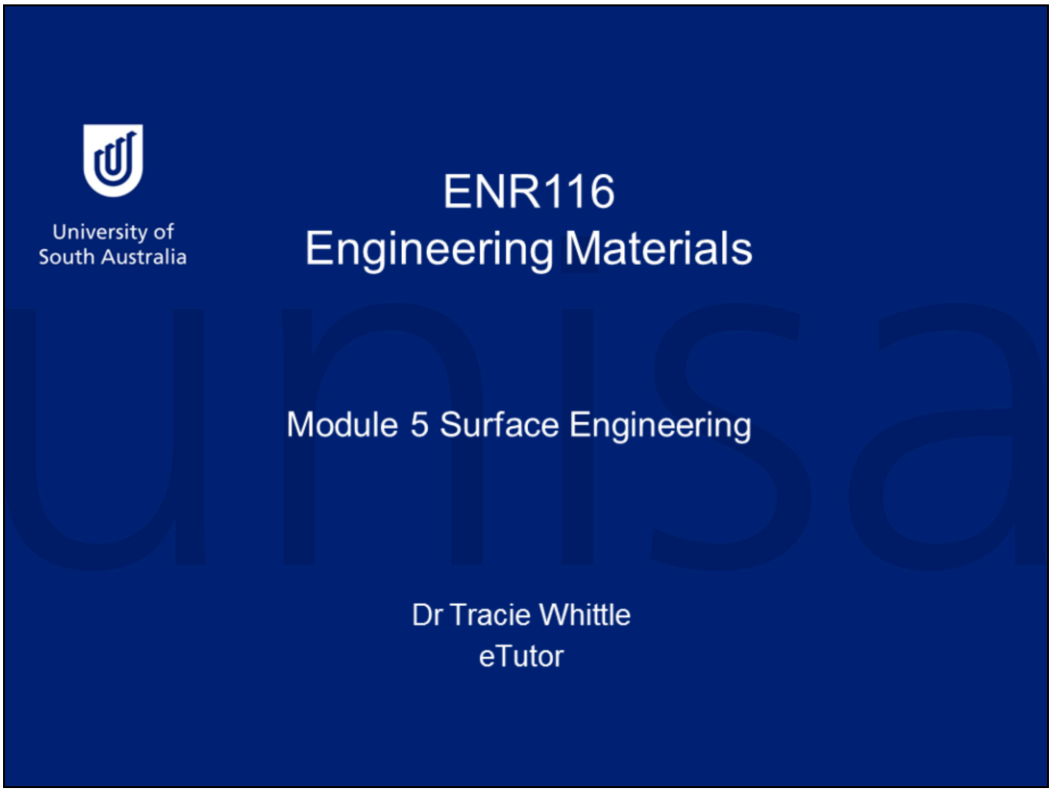

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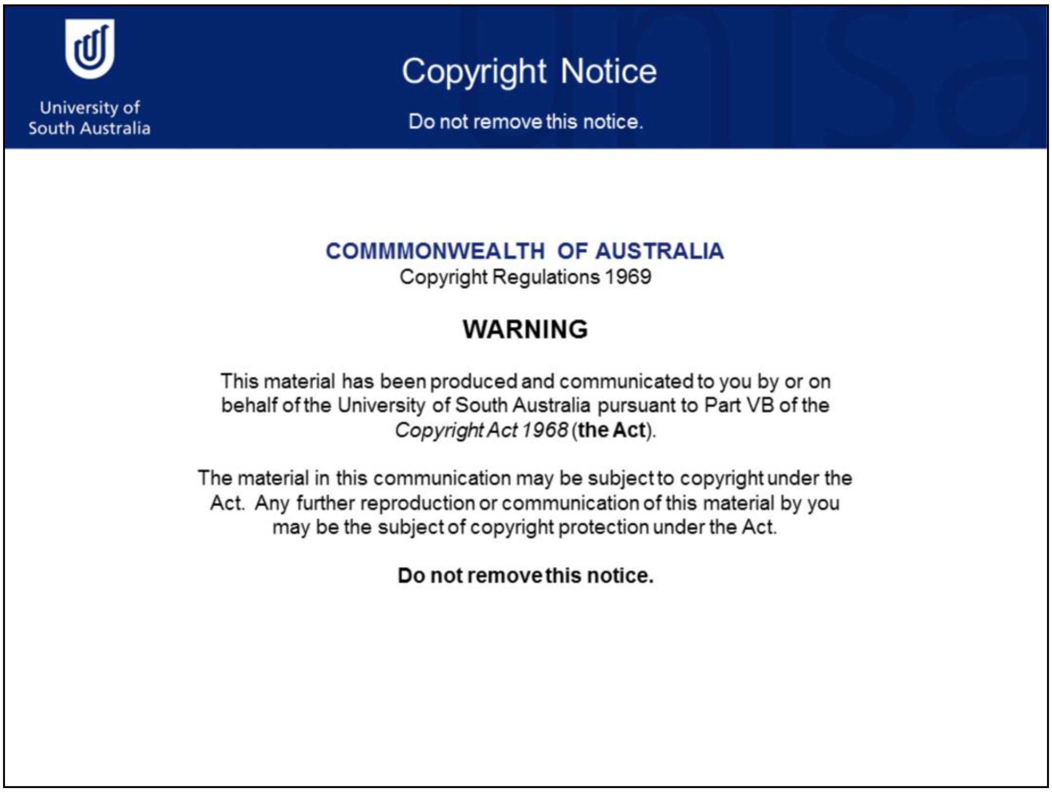
ENR116
Engineering Materials

Module 5 Surface Engineering

Dr Tracie Whittle
eTutor

Welcome to ENR116, Module 5, Surface Engineering.



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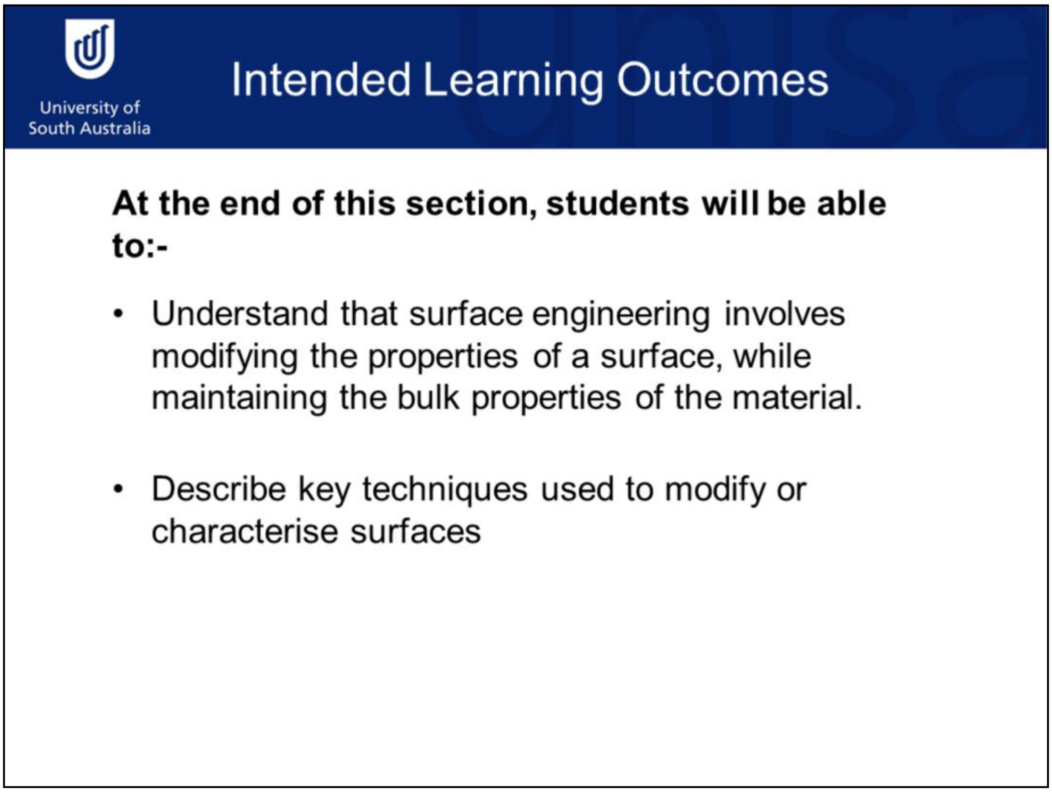
Surface Engineering



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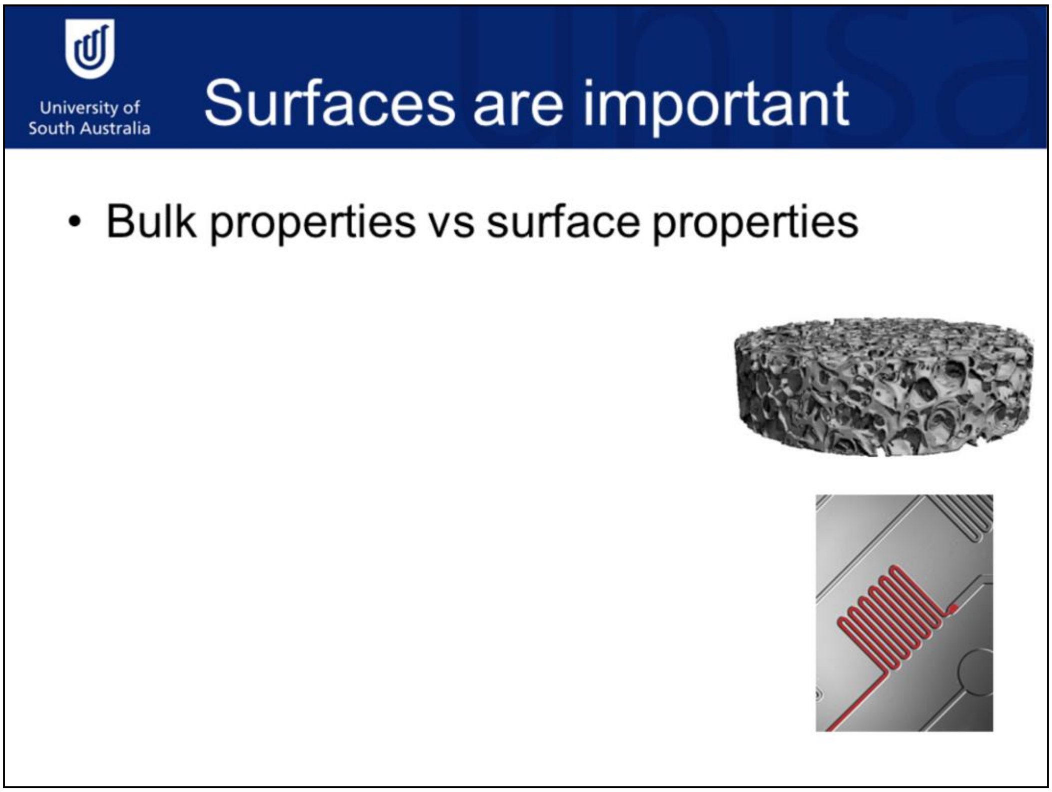
Intended Learning Outcomes

At the end of this section, students will be able to:-

- Understand that surface engineering involves modifying the properties of a surface, while maintaining the bulk properties of the material.
- Describe key techniques used to modify or characterise surfaces

The intended learning outcomes of this lecture summary are: for students to understand that surface engineering involves modifying the properties of a surface, while maintaining the bulk properties of the material.

And, to be able to describe key techniques used to modify or characterise surfaces



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Surfaces are important

- Bulk properties vs surface properties

There is a difference between the bulk properties of a material and those of the surface.

Surface properties are particularly important both because we interact with surfaces but also, because surfaces are the interface between the material and its environment.

This image is of synthetic bone, which can be used as an implant in the case of a bad break.

The material is porous, and has been carefully designed so that it’s bulk properties mimic real bone exactly.

However, as this material is going into the human body, its surface also needs to be exactly what is expected in order to stop the implant being rejected. The surface needs to be completely biocompatible.

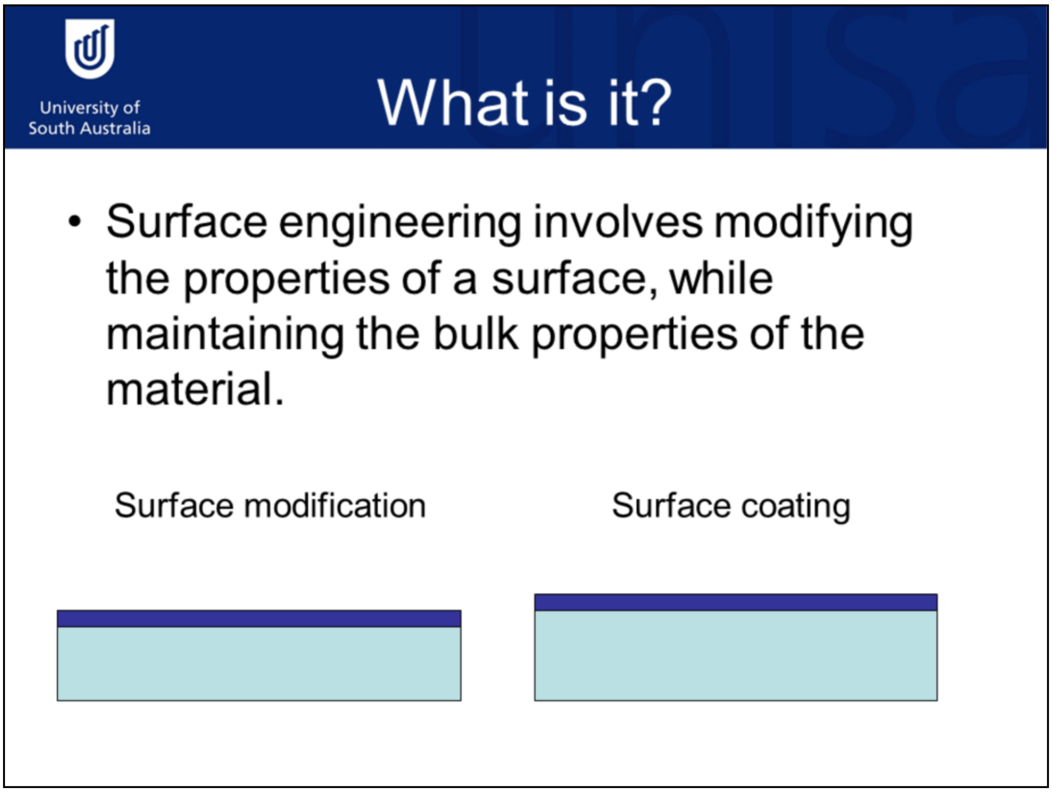
A current trend in technology is the drive towards smaller devices. As the size of a system reduces, we see an increase in surface to volume ratio.

This image is of a Lab on a chip system which contains some very small microchannels.

These channels host specific chemical reactions.

Given that the surface area is very high relative to the size of the system, we need to be sure that the surfaces here are non fouling and compatible with the reactions taking place within the system.

Finally, the drive for new and novel materials obviously necessitates a need for new and novel surfaces with specific properties.



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What is it?

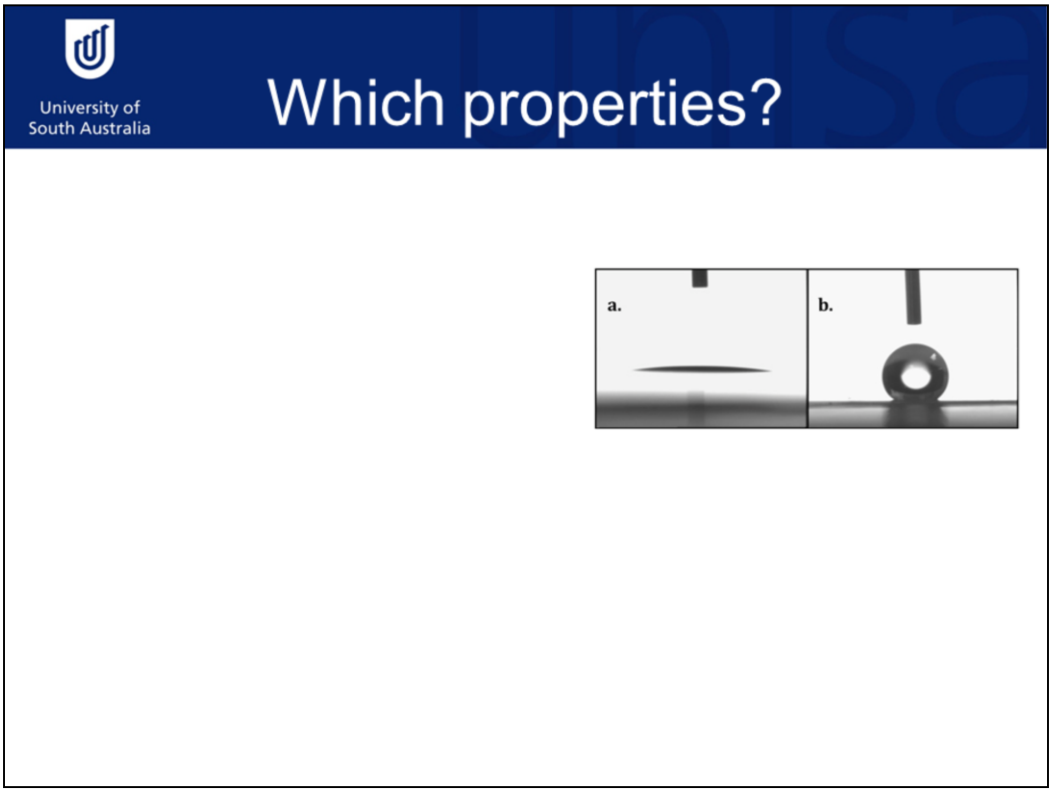
- Surface engineering involves modifying the properties of a surface, while maintaining the bulk properties of the material.

Surface modification

Surface coating

So, what is Surface Engineering? Surface Enginering involves modifying the properties of a surface, while maintaining the bulk properties of the material.

There are two ways of doing this. We can modify an existing surface, as shown in this illustration, or, we can build up a surface coating on top of an existing material, effectively create a new surface with the properties we want.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Which properties?

So, what sort of properties might we want to change?

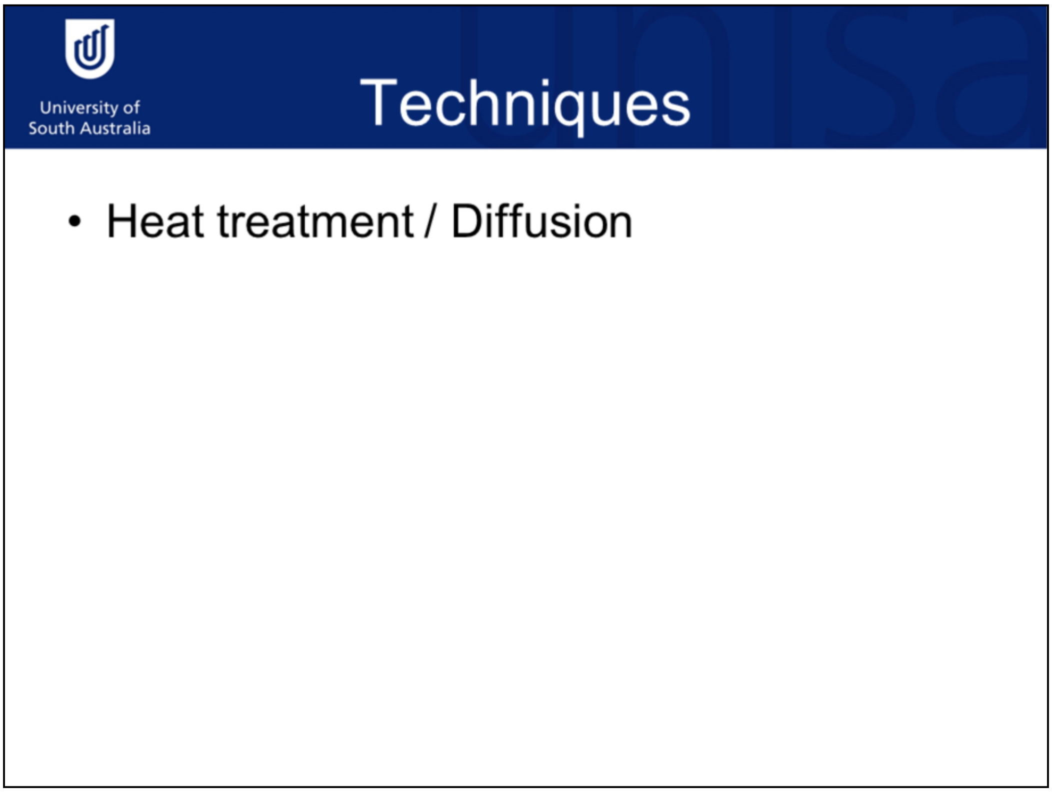
The most common are surface hardness, for example we may wish to make surfaces very hard compared to the bulk, surface roughness and friction and wettability.

In the image here you can see water beading on a surface that has been treated to reduce its wettability.

Optical and reflectivity – a mirror is a simple example of this.

Basic mirrors are glass with a surface coating such as aluminium.

Finally, we have chemical functionality. Other examples are corrosion protection or water sealing.



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Techniques

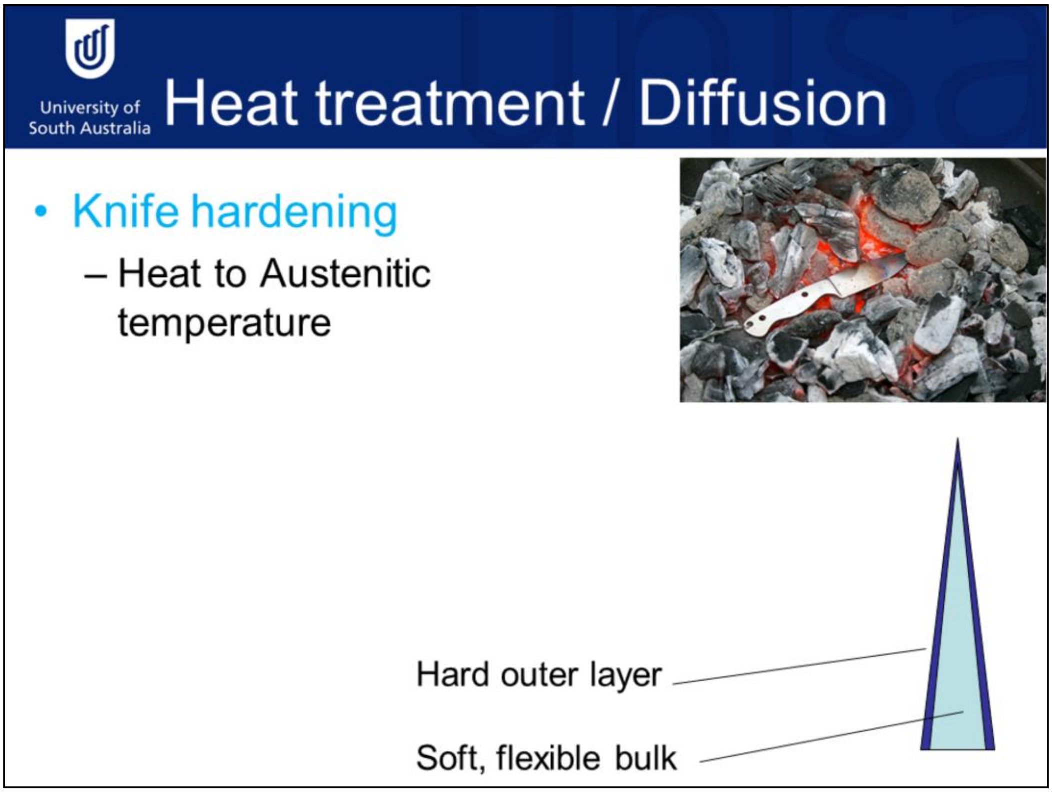
- Heat treatment / Diffusion

We’ll now take a brief look at some of the techniques that might be used to modify a surface.

There are literally hundreds of techniques available and many variations, so here we’ll just be looking at a few key examples.

Heat treatment and diffusion are frequently used, and have been covered previously in the this course.

Ion bombardment and sputtering are both plasma based techniques, and finally, polymeric coatings involve apply thin layers of polymer materials to a surface.



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Heat treatment / Diffusion

- Knife hardening
  - Heat to Austenitic temperature

Hard outer layer

Soft, flexible bulk

We'll start with heat treatment and diffusion.

In the image here you can see a knife being heated in a charcoal fire.

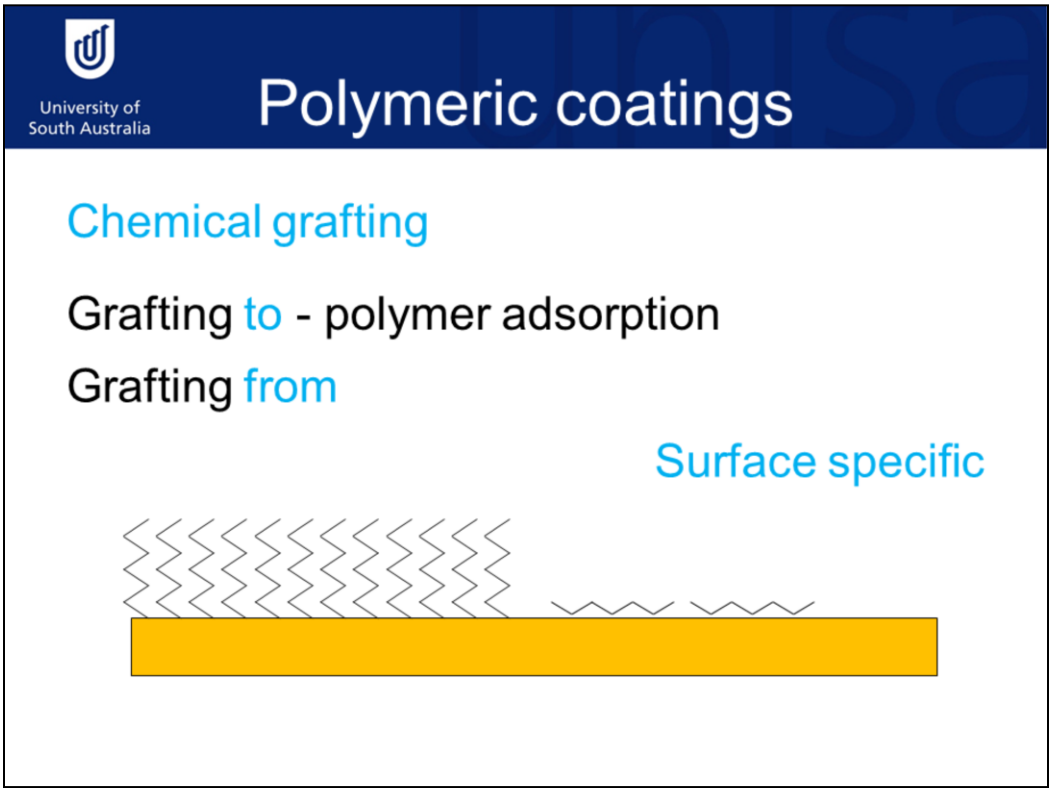
This is a simple means of hardening. By heating the knife to its austenitic temperature and then quenching. surface martensite is formed.

Martensite is very hard and brittle so it helps to keep the knife edge sharp, but because it is also a very thin layer, it allows the knife to maintain some flexibility.

An alternative means of hardening the knife would be to hold in the same charcoal fire at 1000C for about 24hrs.

In this technique, carbon diffuses from the graphite into the steel, increasing the C content and subsequently hardening the surface.

A drawback of this technique is though is that it increases susceptibility of the surface to corrosion.



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Polymeric coatings

Chemical grafting

Grafting to - polymer adsorption

Grafting from

Surface specific

Polymeric coatings. We’ve covered polymers in some detail in earlier lecture summaries, but only in the sense of bulk materials.

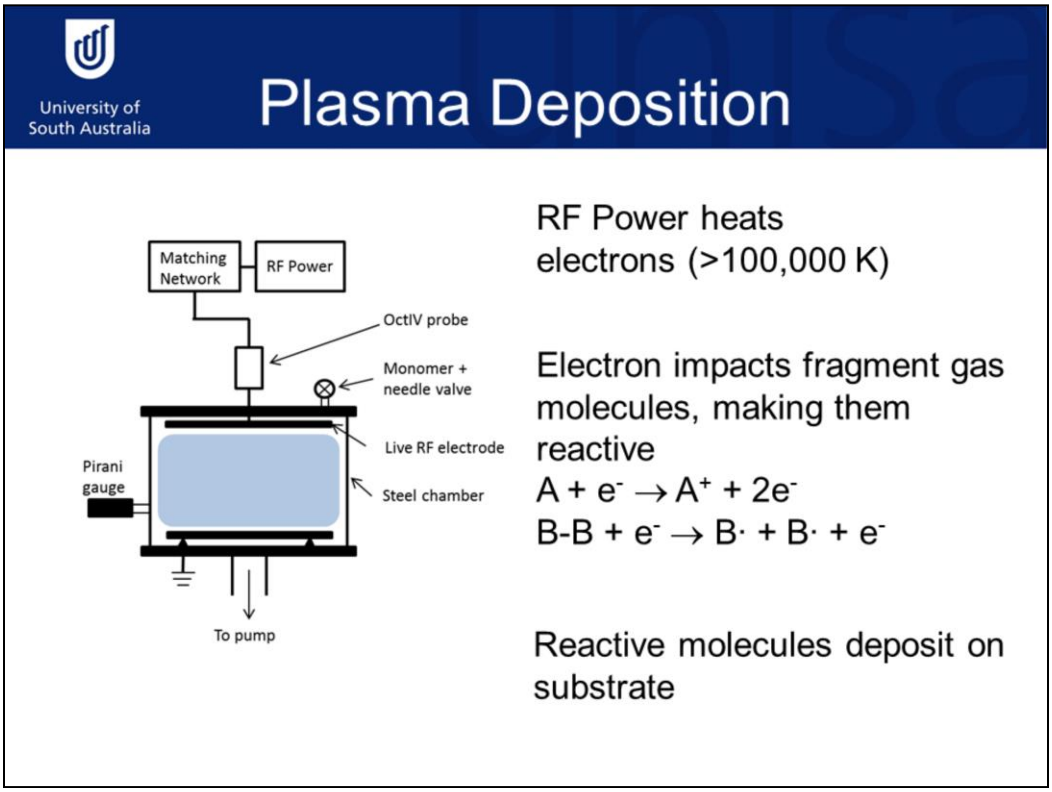
Here we are interested in the fact that polymers with specific properties can be used to tailor the chemistry of a surface. Polymers are often used to modify the wetting properties of a surface.

Chemical grafting is the term used to describe the addition of polymer chains onto a surface.

In the grafting to mechanism, polymer chains adsorb onto the surface from solution.

In the grafting from mechanism, the polymer chain is initiated and propagated at the surface. Grafting from techniques are favoured over polymer adsorption for a number of reasons; including greater control over the location of the polymer and better stability in the final product.

A major problem with polymer coatings as a technique, however, is that they are very surface specific.



Plasma Deposition

RF Power heats electrons (>100,000 K)

Electron impacts fragment gas molecules, making them reactive

$A + e^- \rightarrow A^+ + 2e^-$

$B\text{-}B + e^- \rightarrow B\cdot + B\cdot + e^-$

Reactive molecules deposit on substrate

Plasma deposition is a way of creating very thin polymer- like layers. A major advantage of plasma deposition is that it can be used to coat most surfaces and shapes, provided that the material can tolerant a vacuum.

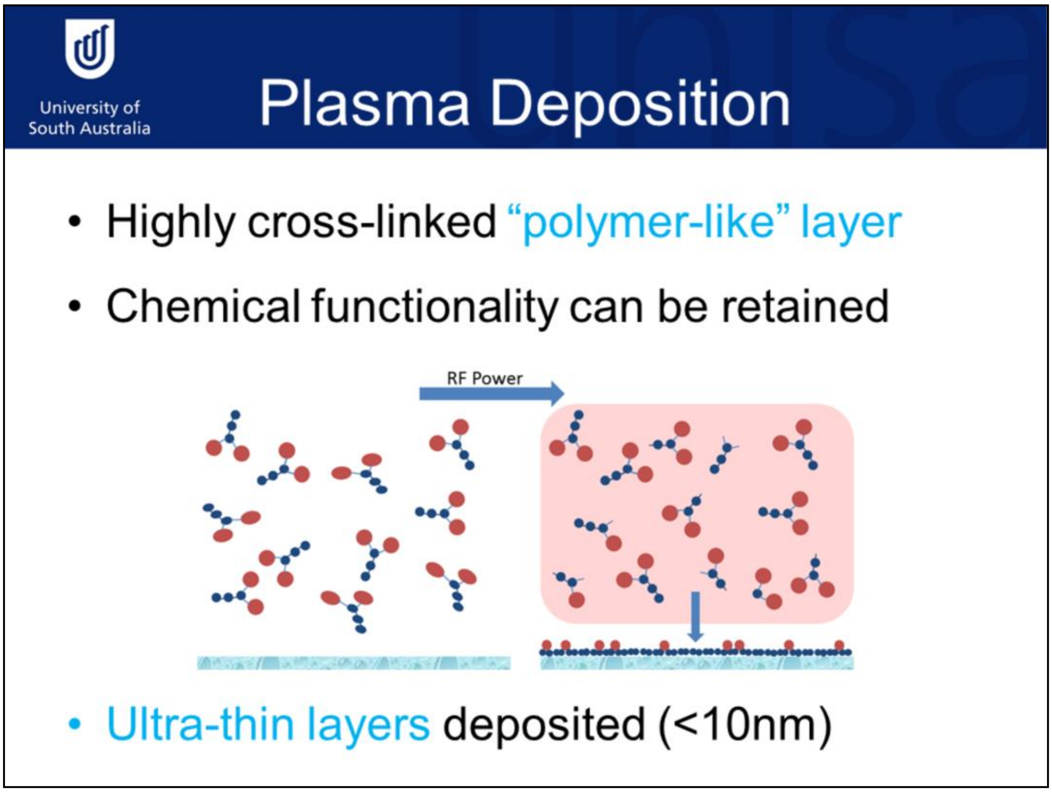
In plasma deposition, an RF source is applied to an electrode, generating positive ion and negative electron pairs.

The field strength across the system drives these apart.

The electrons speed up in field, gaining energy and heating up to around 30,000K and as high as 100,000K.

With this energy the electron can strike other atoms and ionise them, creating another positive ion and electron pair. This new electron subsequently heats up and the process continues.

Molecules within the system may be broken open in this manner, creating radicals. These are very reactive and will react with any surface they collide with, creating a polymeric type deposit. Plasma deposition is most often used with organic molecules such as acrylic acid.



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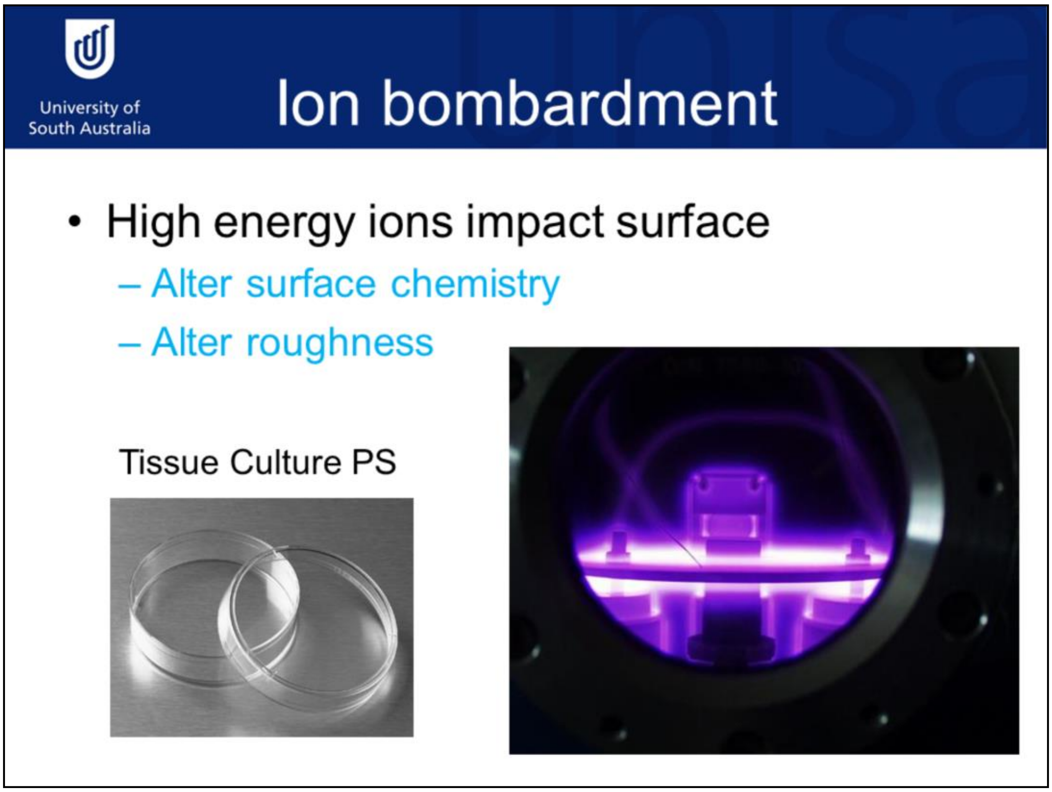
Plasma Deposition

- Highly cross-linked "polymer-like" layer
- Chemical functionality can be retained

- Ultra-thin layers deposited (<10nm)

This schematic shows an organic layer, such as acrylic acid.

When the molecules fragment in the plasma, some will recombine and some don't, creating complex, cross linked, polymer like layers on the surface. These films retain some chemical functionality. The red dots in the illustration might be acid groups, alcohols etc. These plasma polymerised layers are ultra thin, typically less than 10nm.



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Ion bombardment

- High energy ions impact surface
  - – Alter surface chemistry
  - – Alter roughness

Tissue Culture PS

A related method is ion bombardment.

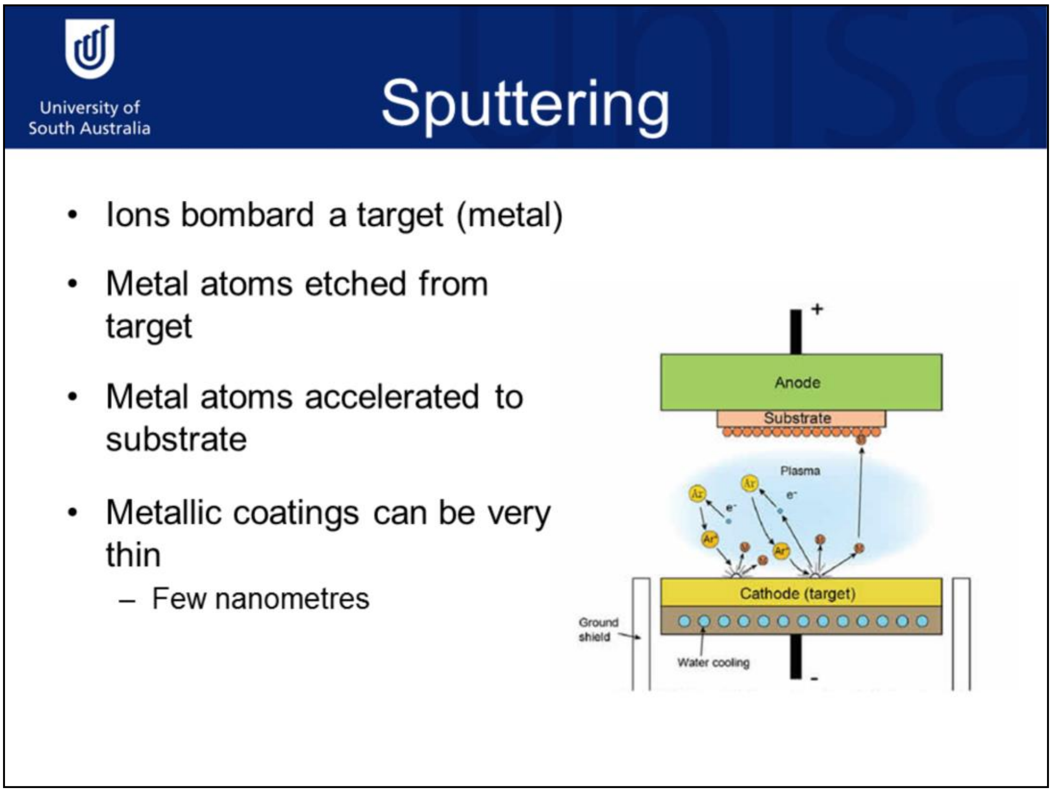
Here an inert plasma, such as He or Ar, is used to accelerate ions onto surface.

These ions hit surface with a lot of energy, and alter the surface chemistry by breaking bonds or implanting atoms. The surface roughness is changed by etching.

Tissue culture polystyrene is an example of a material that has arisen from this surface treatment.

Tissue culture used to be done on glass, but glass is heavy, expensive and really, not that a good a surface for growing cells.

In 1940s PS emerged as a cheaper, lighter alternative, but the surface was still not favoured by cells. In the 1970s, polystyrene petri dishes were treated with an air plasma. This process incorporated more nitrogen and oxygen into the surface and improved the wettability, making it an ideal surface for growing cells.



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Sputtering

- Ions bombard a target (metal)
- Metal atoms etched from target
- Metal atoms accelerated to substrate
- Metallic coatings can be very thin
  - Few nanometres

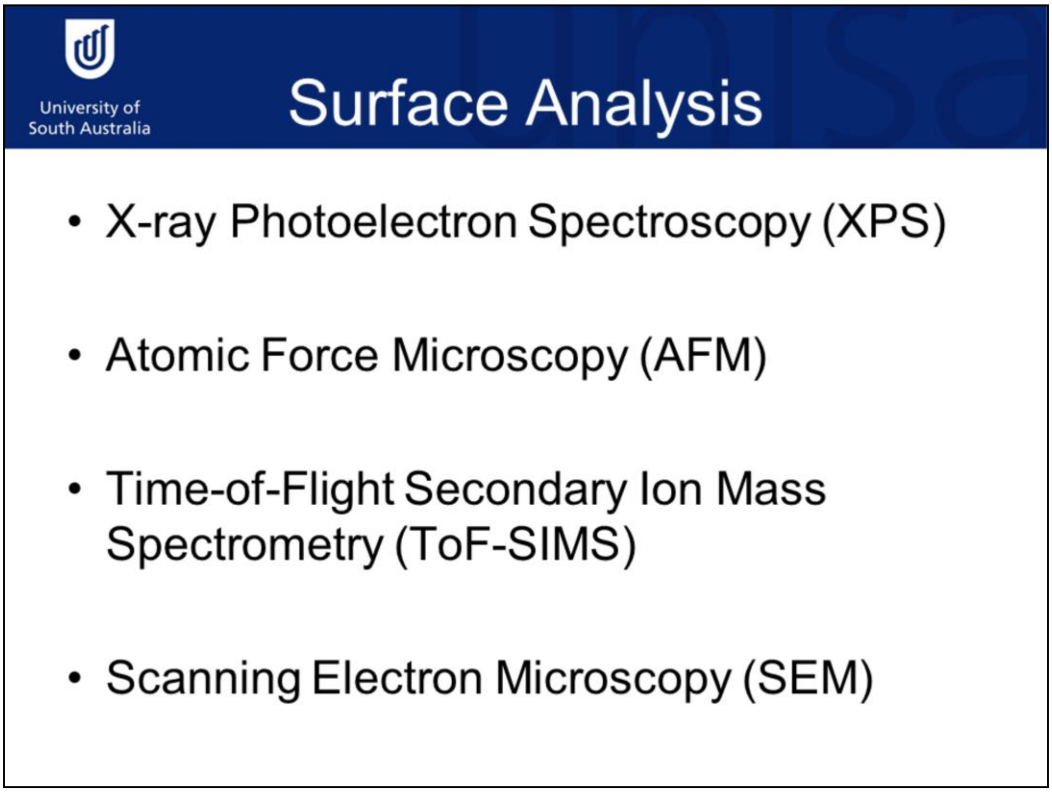
Sputtering is a second related method.

Sputtering is most often used with metals.

Here a plasma is generated with the metal as the cathode.

The system is biased negatively.

Positive ions then hit the surface, etching the cathode and liberating these atoms. The now free metal atoms are accelerated, strike the substrate and create a thin coating of metal. The coatings are typically just a few nm thick. The substrate is often rotated to ensure even coverage. By using a number of different cathodes with different source metals, it is possible to create more complicated layered structures,.



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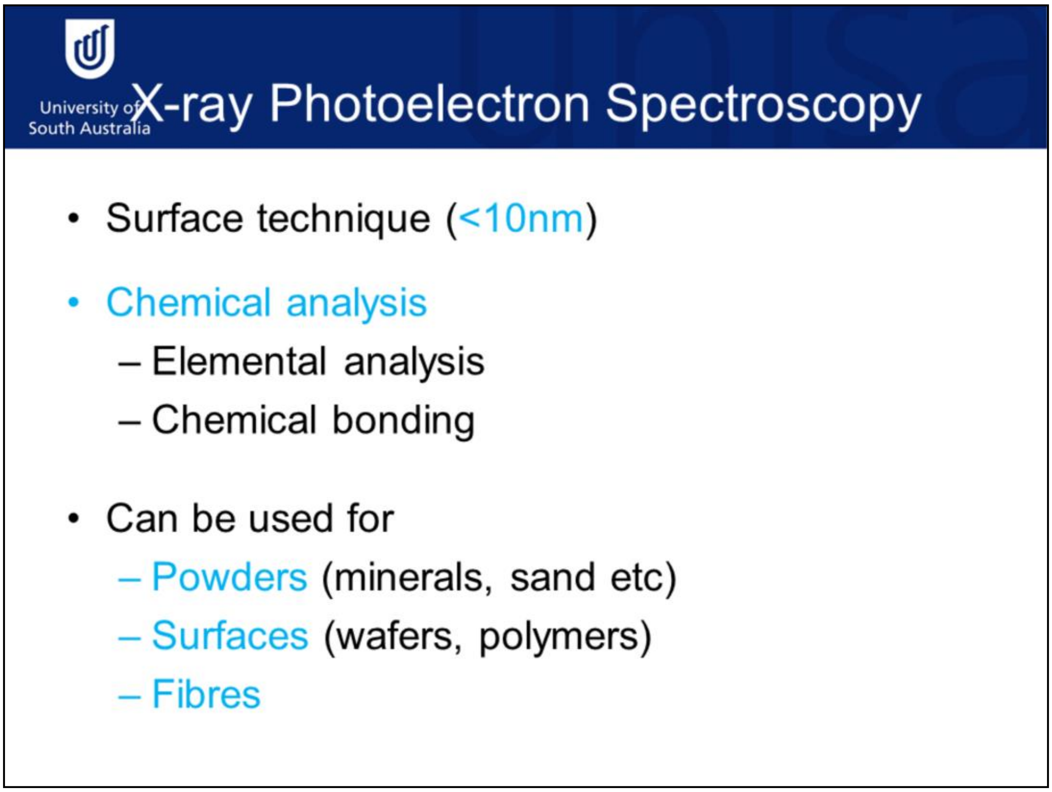
Surface Analysis

- X-ray Photoelectron Spectroscopy (XPS)
- Atomic Force Microscopy (AFM)
- Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)
- Scanning Electron Microscopy (SEM)

Having explored a few techniques for surface engineering, we are now going to look at how we can characterise a surface once we have it.

The term surface analysis describes the methods used to do so. Surface analysis is different from bulk analysis, as they need to analyse thin layers with unique properties from the bulk material.



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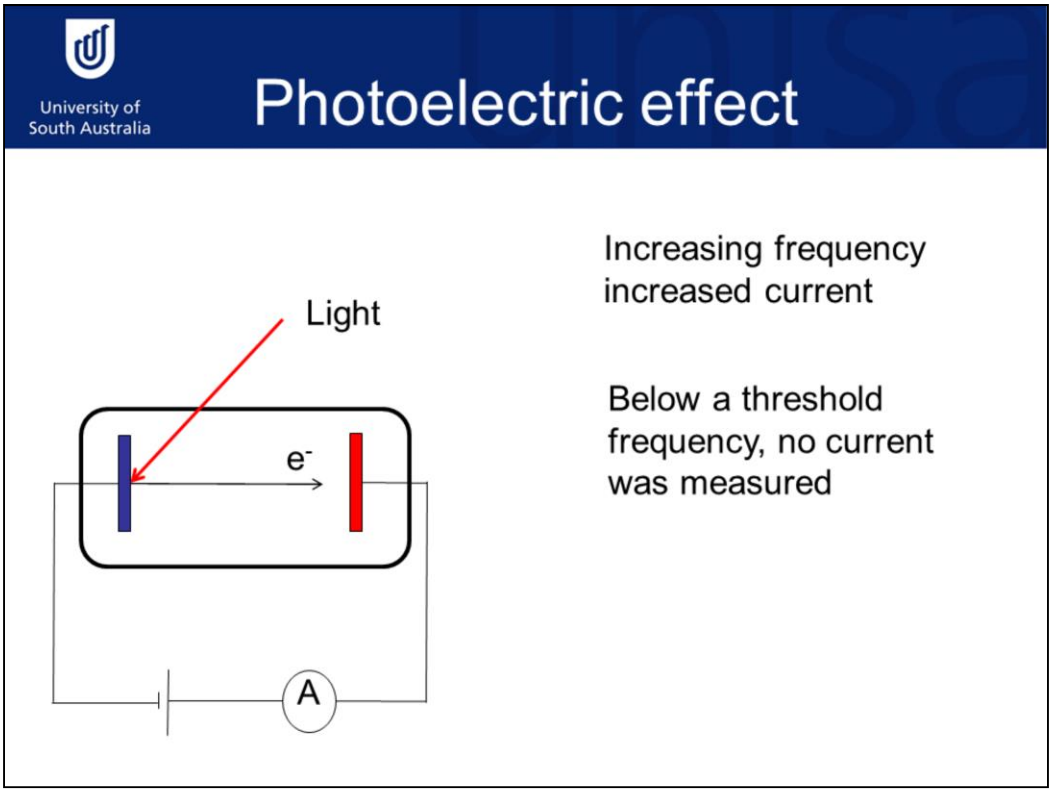
X-ray Photoelectron Spectroscopy

- Surface technique (<10nm)
- Chemical analysis
  - Elemental analysis
  - Chemical bonding
- Can be used for
  - Powders (minerals, sand etc)
  - Surfaces (wafers, polymers)
  - Fibres

Xray photoelectron spectroscopy is a technique used for the chemical analysis of surfaces.

The technique is very surface specific, providing information on the top 10nm of the surface only. XPS offers elemental analysis, plus some information about chemical bonding. It can be used for wide range of substrates, provided they can tolerate high vacuum. It cannot be used with volatile materials.



Photoelectric effect

Increasing frequency increased current

Below a threshold frequency, no current was measured

The history of XPS goes back a long way.

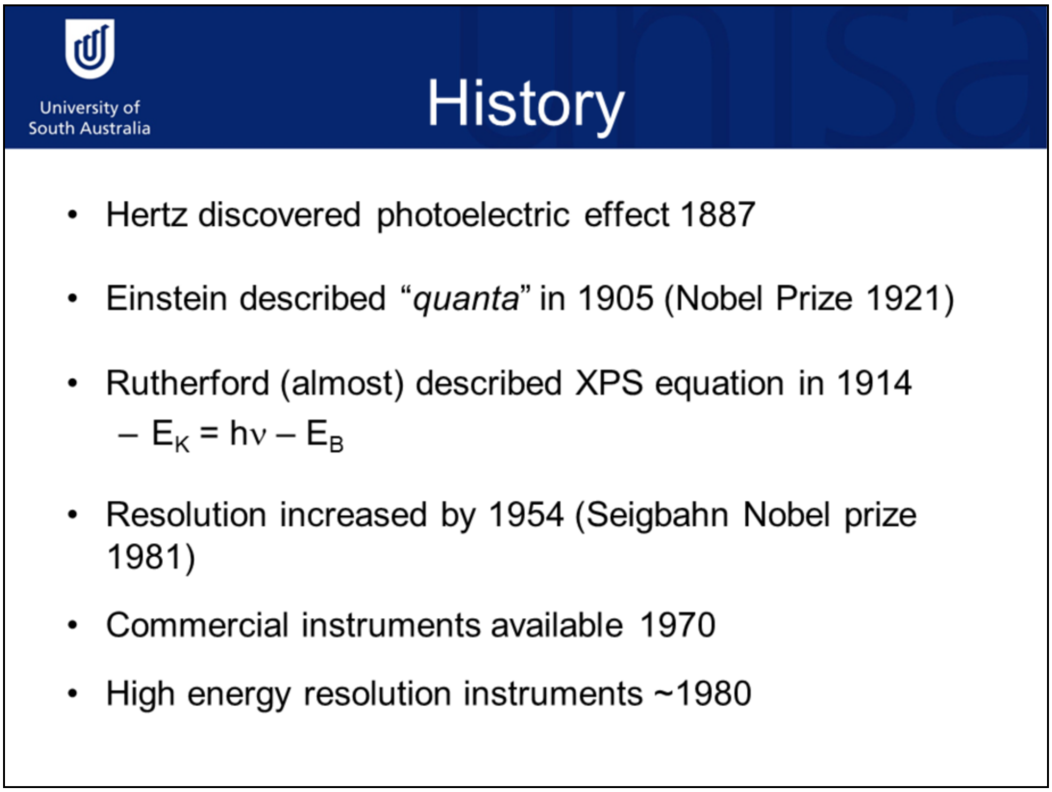
In an early experiment by Hertz, two plates were situated in air with a voltage applied across them.

Hertz was interested in determining the minimum voltage required in order to cause spark to jump across from one plate, to the next?

Hertz worked on his experiment in the dark, but one day some light crept in from a window, and he immediately observed a spark. The light on one plate caused electrons to move from one side to other, generating a measurable current.

Although Hertz didn’t know it at the time, this was a direct consequence of the photoelectric effect.

He went on to see that increasing the frequency of the light increased the current across the plates. Below a threshold frequency, no current was measured.



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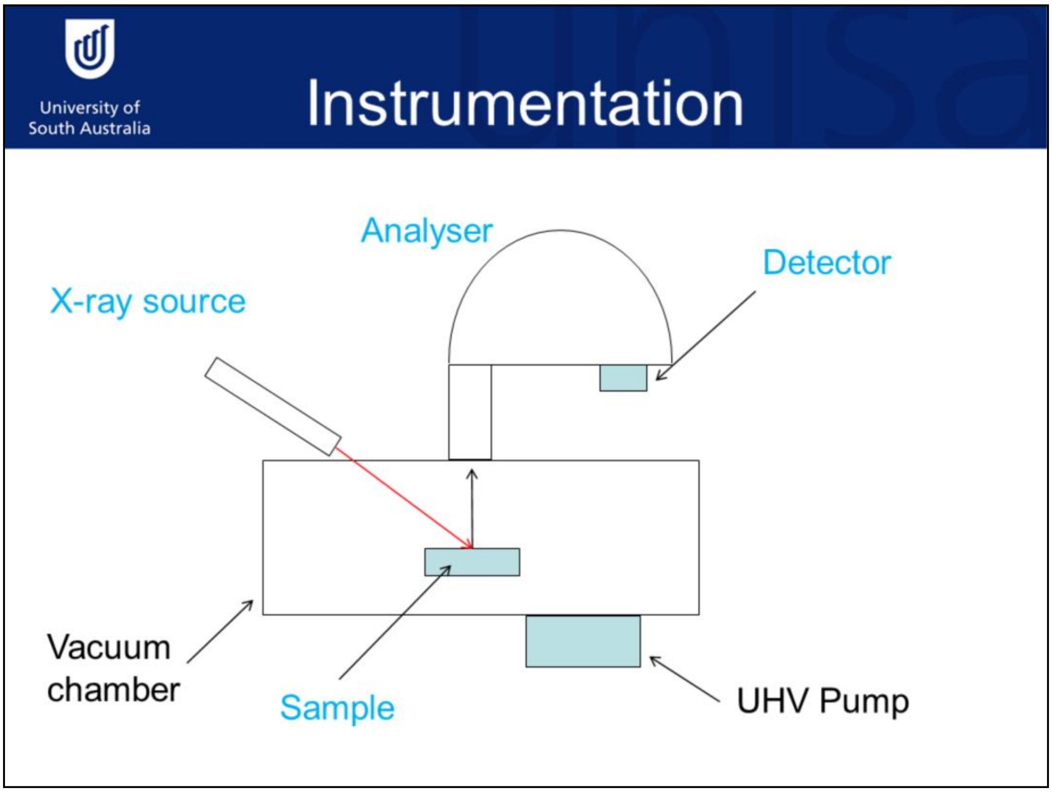
History

- Hertz discovered photoelectric effect 1887
- Einstein described "*quanta*" in 1905 (Nobel Prize 1921)
- Rutherford (almost) described XPS equation in 1914
  - $E_K = h\nu - E_B$
- Resolution increased by 1954 (Seigbahn Nobel prize 1981)
- Commercial instruments available 1970
- High energy resolution instruments ~1980

- Hertz discovered the photoelectric effect in 1887.
- Einstein then won the Noble prize in 1905 for describing quanta, what we now call photons.
- Rutherford then very nearly described the converation of energy equation used in XPS.
- Development of XPS as a technique was then halted due to the World wars, but in 1954 resolution was improved considerably.
- By the 1980s high resolution instruments were available commercially.



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Instrumentation

Analyser

Detector

X-ray source

Vacuum chamber

Sample

UHV Pump

This is a basic outline of an XPS machine. The Xray source, here, irradiates the sample. The electrons pass though the analyser, and into the detector. The entire operation is housed within a vacuum chamber.

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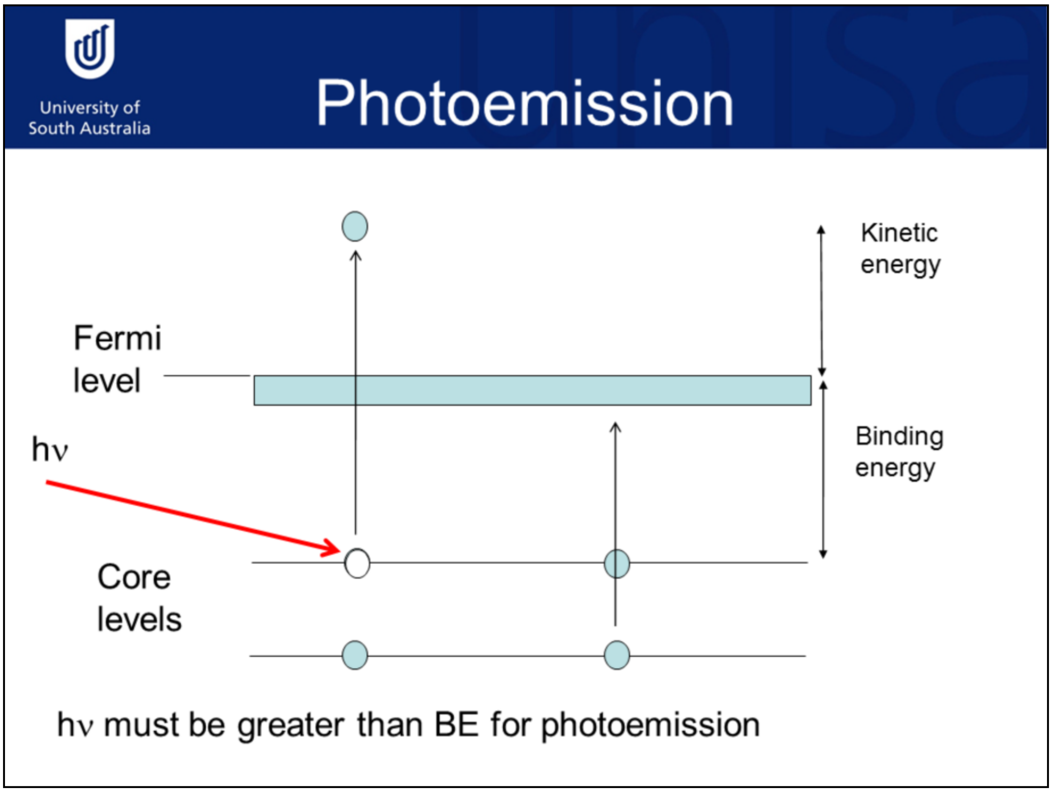
Instrumentation

This is a real XPS. You can see the hemispherical analyser, at the top of the machine, the analysis chamber and the xray gun.



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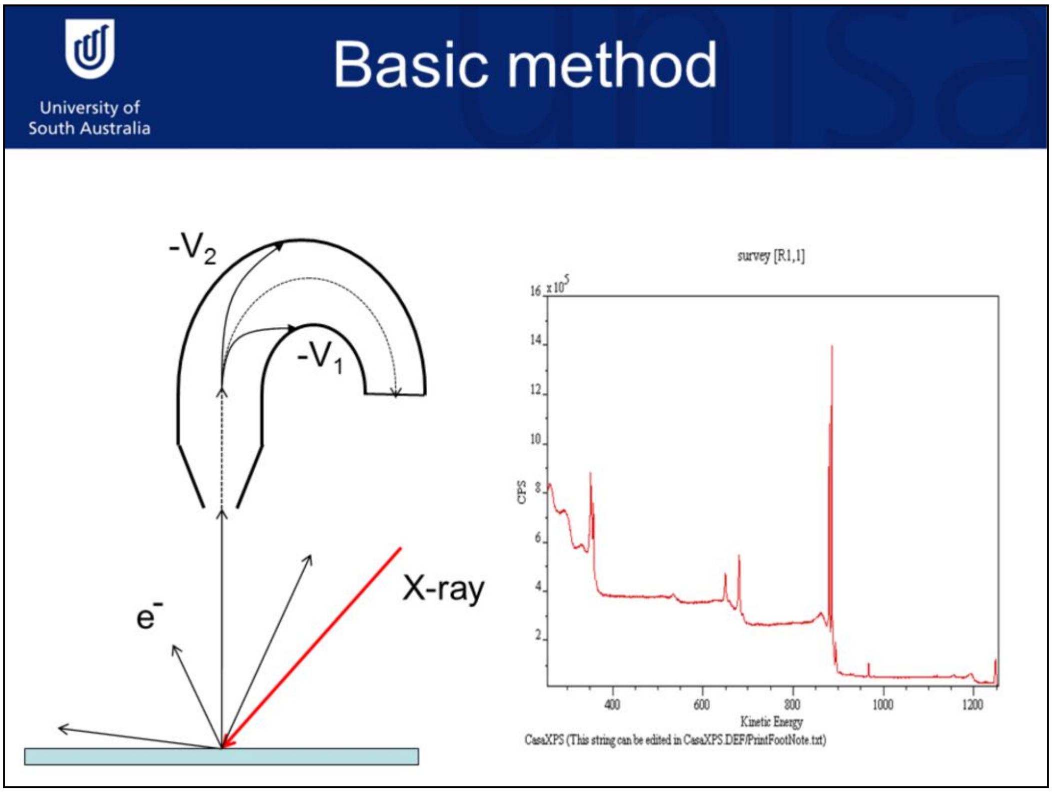
Photoemission

hν must be greater than BE for photoemission

This is what happens in an XPS experiment.

Electrons sit in core levels. The Fermi level is the level at which the electrons are free of the atom.

The sample is irradiated with X-rays, causing the electron to be ejected to the surface, leaving behind a hole. This photoemission process obeys a convservation of energy rule, where the energy of the x-ray radiation is equal to the binding energy of the electron and kinetic energy. We know the radiation energy, and we measure the kinetic energy and number of emitted electrons.   It is therefore a simple matter to determine the BE of the electrons, and this in turn tells us about the elements present, and their bonding environment. The only limitation is that the photon energy, hv, must be greater than the binding energy in order to eject the electron to the surface.



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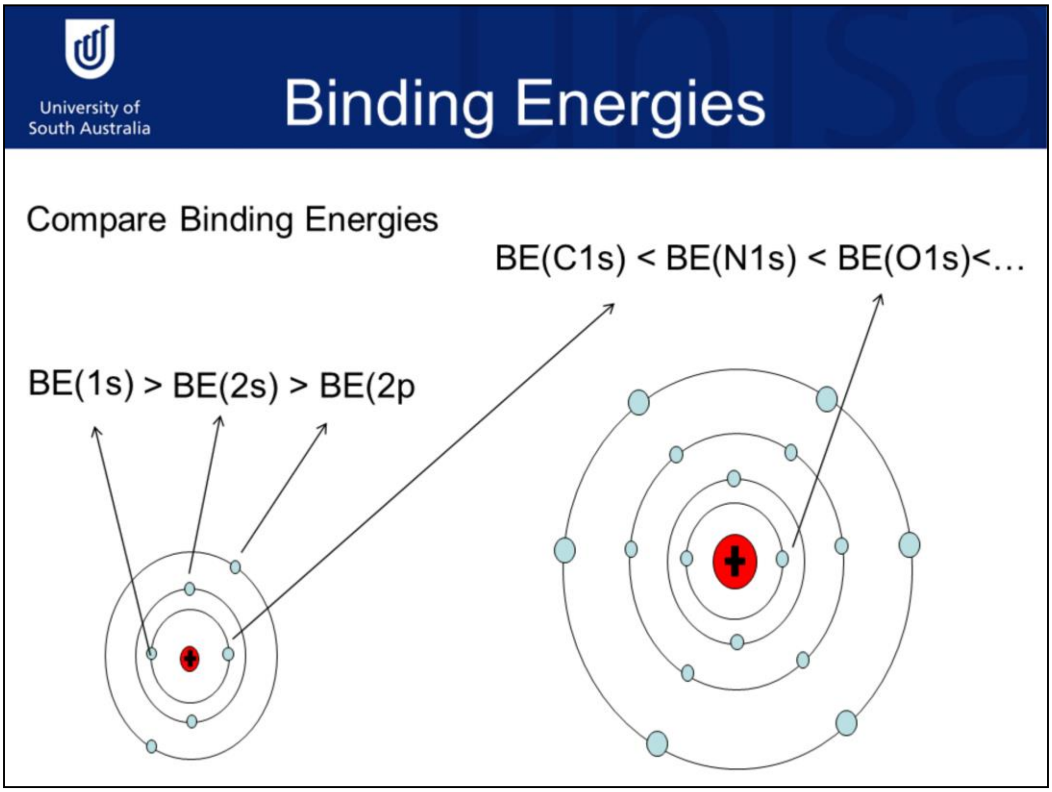
Basic method

This is the basic method of the XPS experiment.

Electrons of all energies fly out from the sample in all directions. Some will pass into the analyser, here.

The plates within the analyser are negatively biased. They act to repel the electrons, and select for electrons of a particular, target energy.

If an electron is too slow it will hit the surface of this plate. If it is too fast, so it has a higher energy than that we are selecting for, it will spin out and hit this plate. Only electrons of the desired energy will pass through and reach the detector. So by carefully selecting the plate voltages it is possible to select for certain KEs and build up a spectrum like this one, with kinetic energy on the x axis, vs electron counts per second on the y axis. Each of these peaks is characteristic of a particular KE, which is turn is characteristic of a particular element and sub shell. You can think of each element has having a unique spectral fingerprint.



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Binding Energies

Compare Binding Energies

BE(C1s) < BE(N1s) < BE(O1s)<…

BE(1s) > BE(2s) > BE(2p

Here we can compare the binding energies of different electrons, and see why there we get some many different peaks in the XPS spectrum.

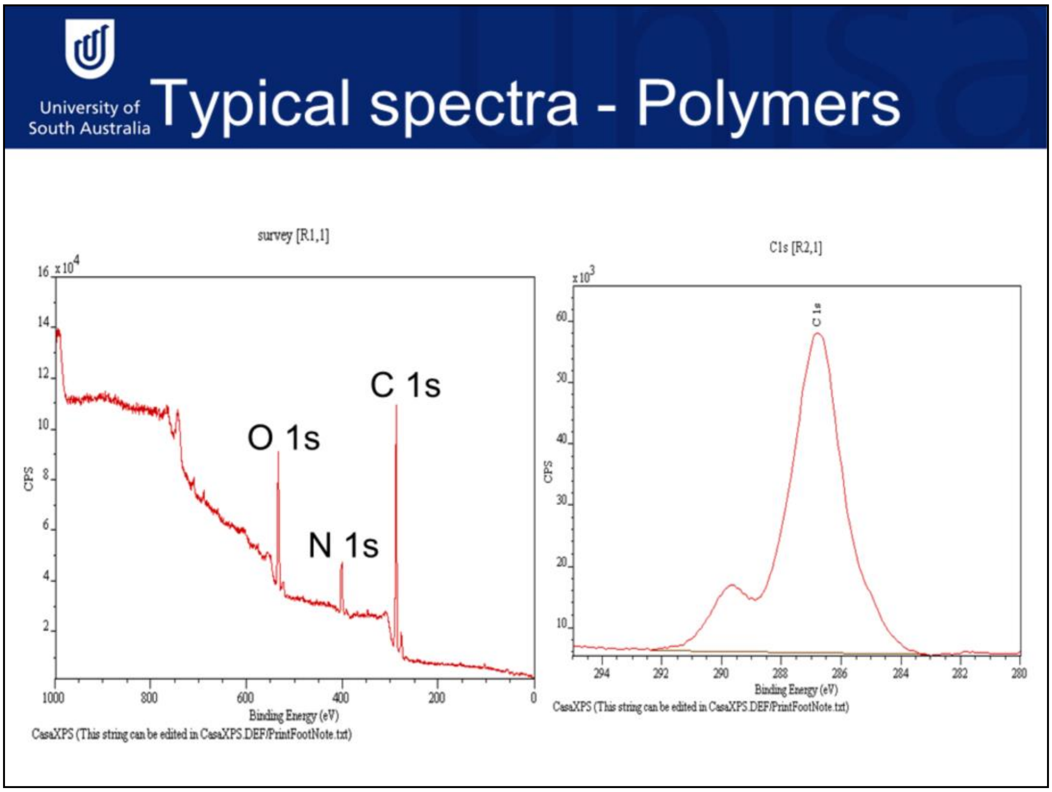
In the Carbon atom here, you can see the electrons in the 1s shell are closest to the nucleus, and are therefore bound tightly.

As you'd expect, they have a much greater BE than electrons in the 2s or 2p shells.

The binding energies also differ between different atoms.

This atom, oxygen, has a greater number of electrons of electrons than the carbon atom, and the nucleus has a greater net positive charge, so we'd expect the 1s electron in oxygen to have a greater binding energy than for the carbon.

These differences in the number of electrons and protons and neutrons between atoms means that many electrons have unique binding energy values, and in fact there not many overlaps at all between peaks in the XPS spectrum.



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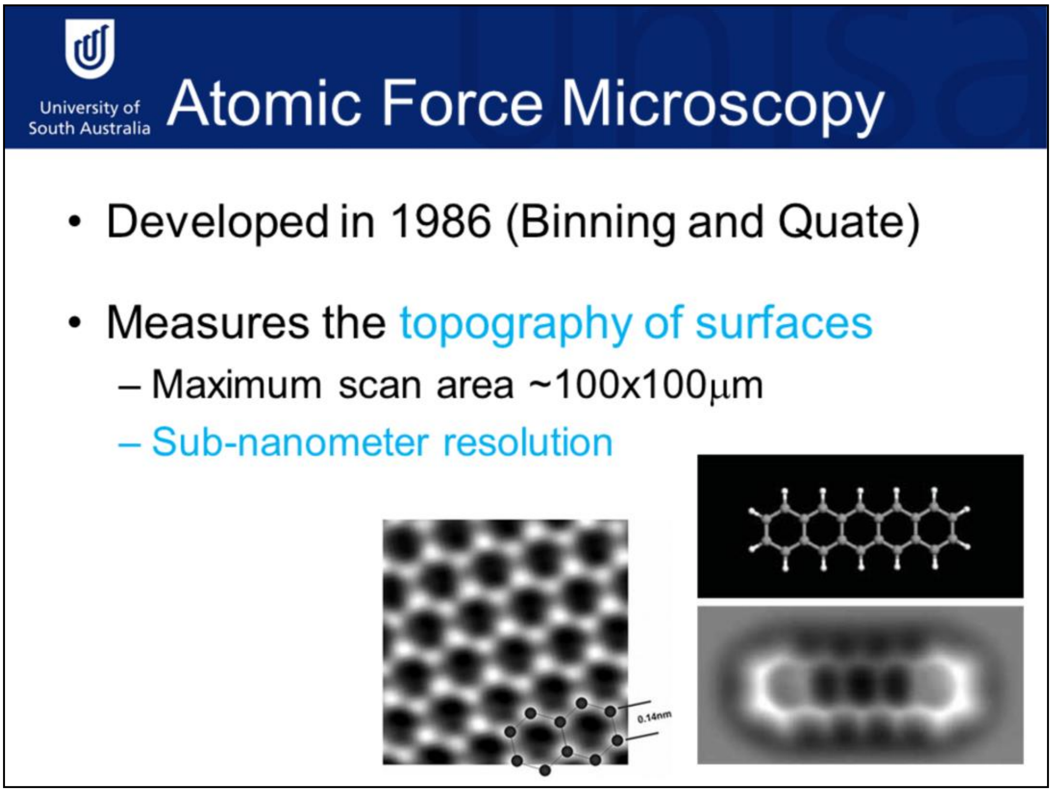
Typical spectra - Polymers

There are some XPS spectra for a typical polymer.

This is nylon.

The x axis data here have been converted to binding energy, rather than kinetic energy.

We can see the characteristic peaks for C1s, N 1s, and O 1s. We can use the height and area of peaks to determine the relative amounts of each element in the sample, which in itself makes XPS a very useful technique. However, the real power is in shape of these peaks, which tells us about the chemical bonding within the surface. This is the high resolution scan of the C 1s peak. These components correspond to C-C, and C-N and C bonded to O. Acid groups, C-O bonds, C-F bonds all give characteristic peaks in the high resolution scan.



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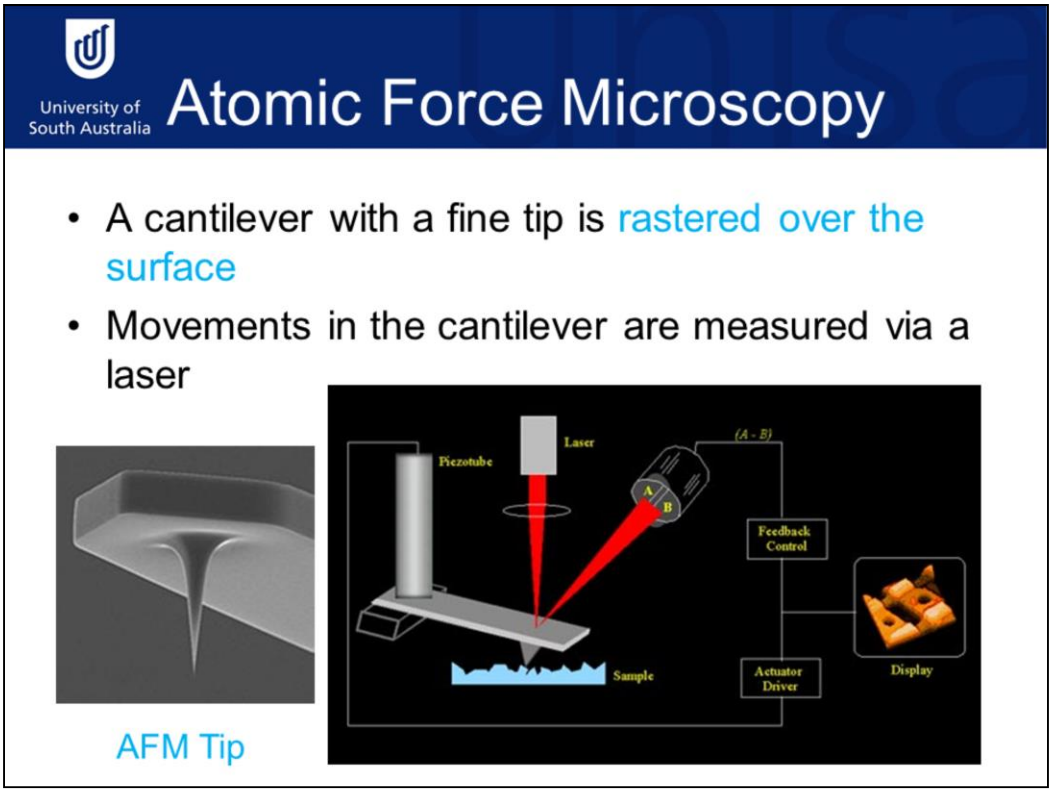
Atomic Force Microscopy

- Developed in 1986 (Binning and Quate)
- Measures the topography of surfaces
  - Maximum scan area ~100x100μm
  - Sub-nanometer resolution

We’re now going to take a look at atomic force microscopy, or AFM. AFM was developed in 1986. It was initially an extremely difficult technique, requiring some serious expertise and equipment, but now AFM instruments are commercially available and are a standard feature in most surface analysis labs. The AFM is capable of imaging very small areas, typically the maximum scan area is in the region of 100 microns square, with sub nanometer resolution.



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Atomic Force Microscopy

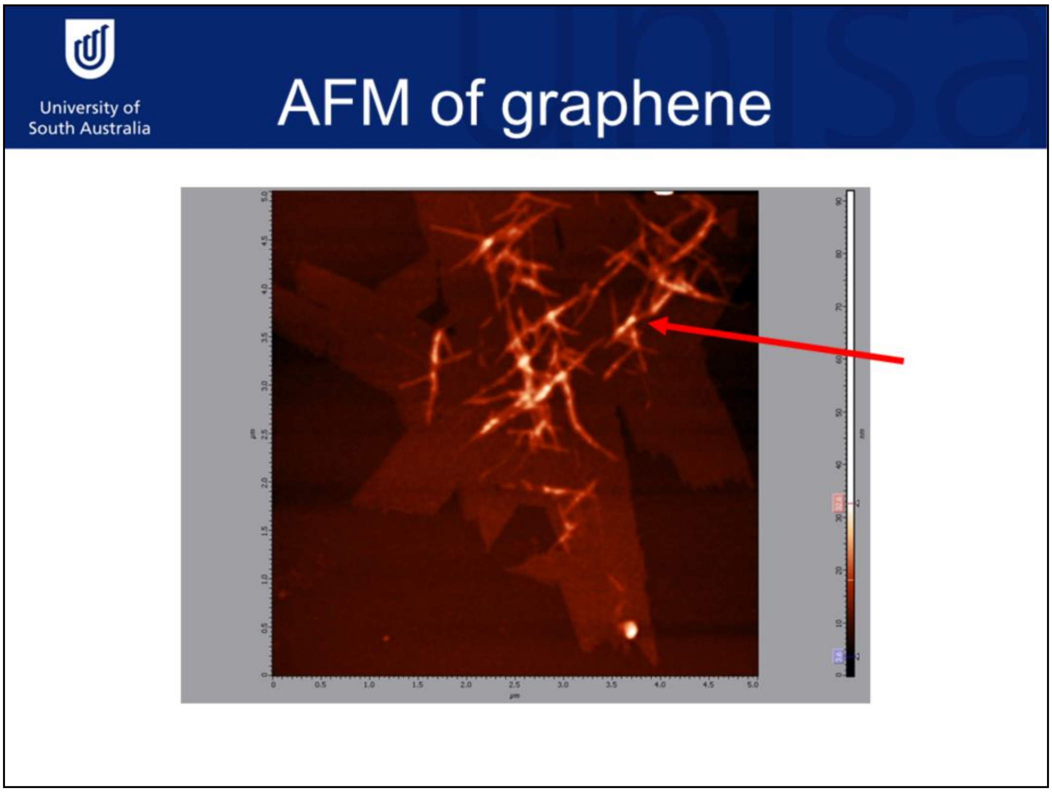
- A cantilever with a fine tip is rastered over the surface
- Movements in the cantilever are measured via a laser

AFM Tip

You can imagine the AFM working almost in the way that a record player does.

It comprises a a cantilever with a very fine tip – typically, with a radius of just a few nm – which is rastered over the sample surface.

Changes in the position of the cantilever are detected then using a laser. The laser is bounced off the reflective back of the cantilever onto a detector. The changes in position are monitored and used to build up an image of the topography of the surface.



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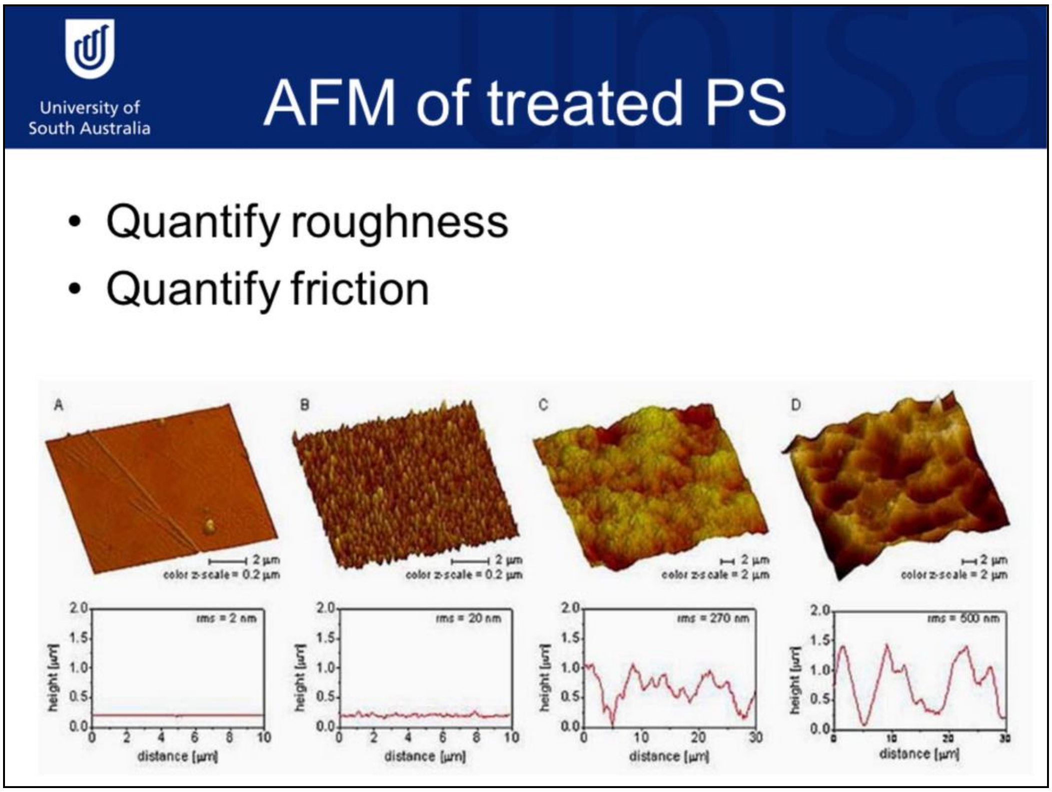
AFM of graphene

There is an example of a AFM of graphene. The individual graphite sheets here are only about 1 atom thick, yet you can see these steps from one sheet to the next clearly. The bright lines show areas where the surface has been damaged.



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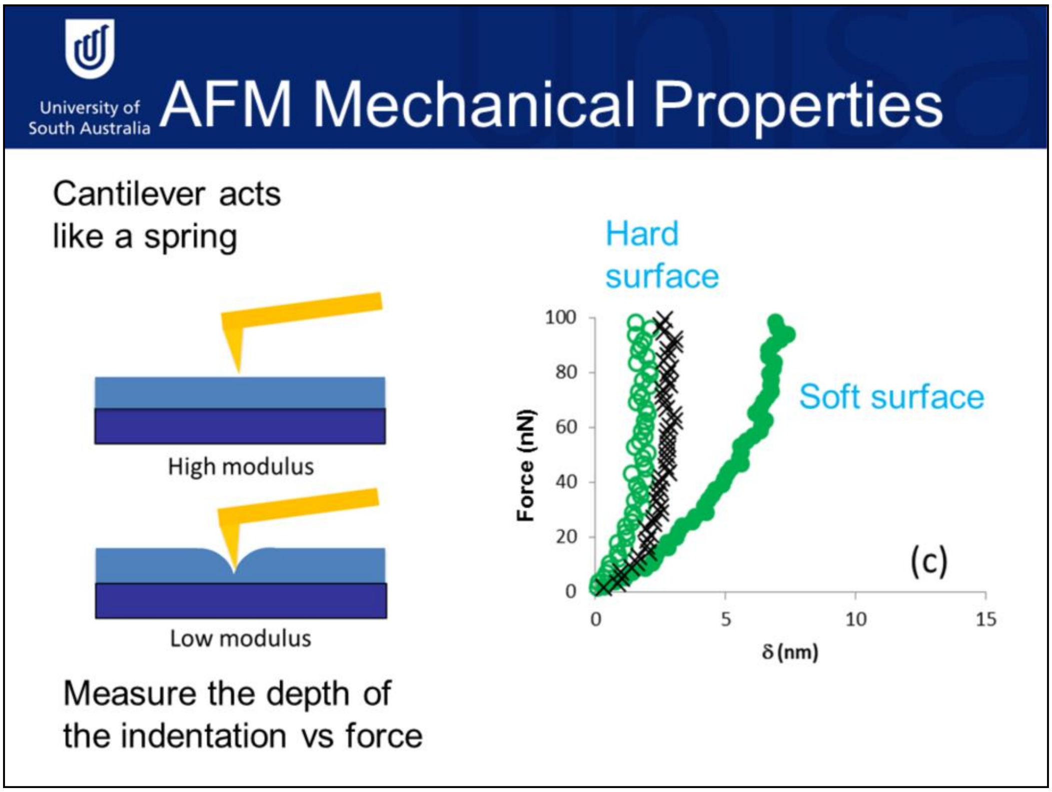
AFM of treated PS

- Quantify roughness
- Quantify friction

The images here show how the topography of tissue culture PS changes with etching time. Earlier in this summary we described how PS may be etched to prepare the surface for tissue culture. As the etch progresses, the surface becomes progressively rougher. We can quantify these changes using the AFM images, by measuring a value known as the root mean squared roughness at each time point.

AFM may also be used to monitor changes in the frictional interactions between the tip and the surface. This variant of AFM is known as frictional force microscopy, or FFM.



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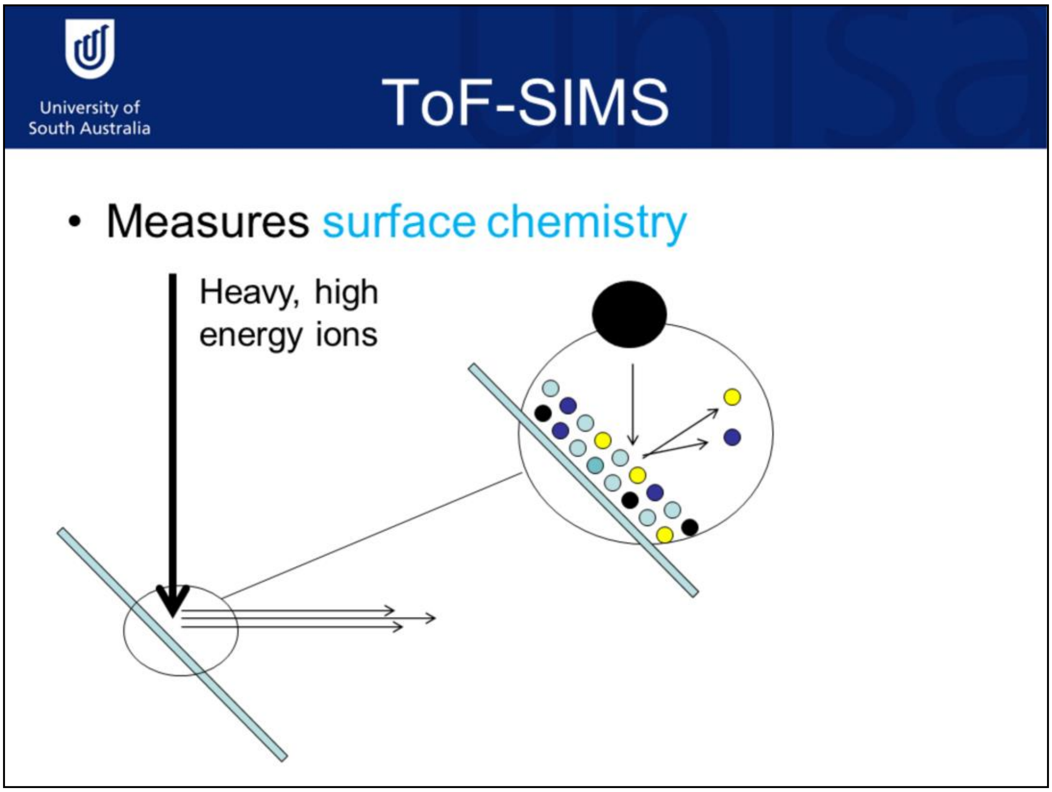
AFM Mechanical Properties

Cantilever acts like a spring

Measure the depth of the indentation vs force

The AFM is also used to measure the mechanical properties of a surface. The cantilever is effectively used to preform a tensile test on thin layers. The cantilever acts like a spring, pushing down. Soft surfaces will yield under the applied load, and the depth of the resulting indentation can be measured.

The plot here shows the magnitude of the force applied to the surface and the resulting indentation size. For a hard surface, the relationship is an almost straight line up and down, but for softer surfaces the change is more gradual. These data can be fitted and used to yield a value for the elastic modulus of the surface.



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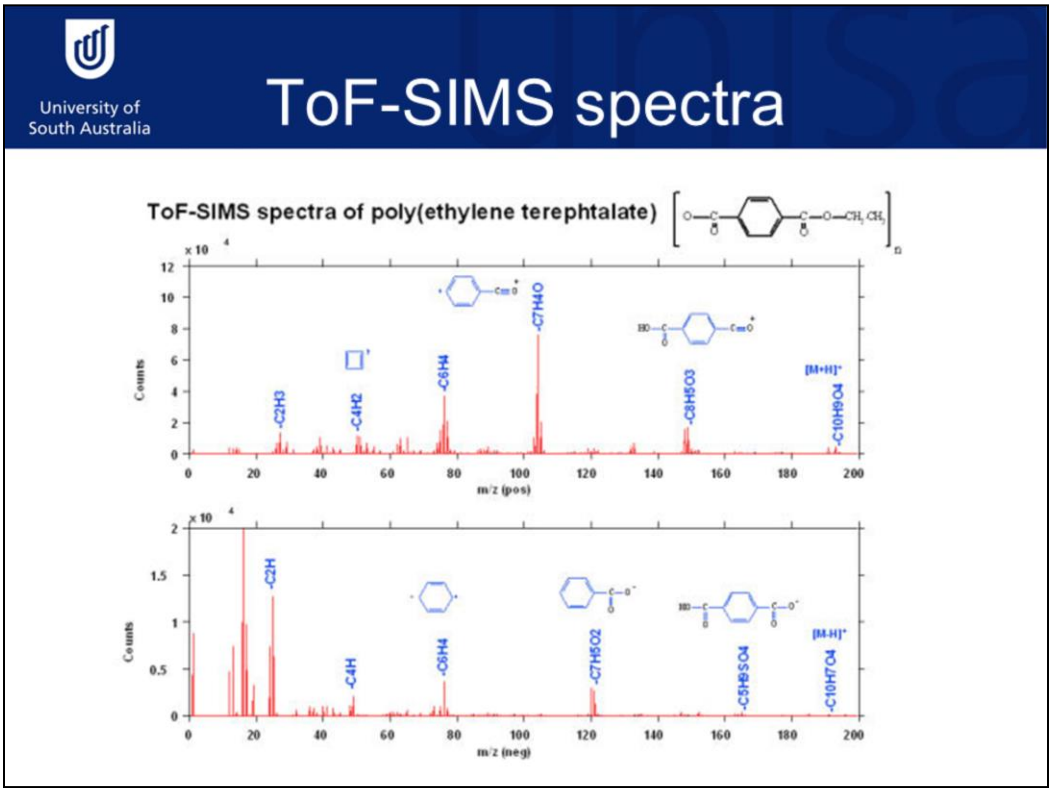
ToF-SIMS

- Measures surface chemistry

The next technique we will consider is time of flight secondary ion spectrometry, or ToF SIMs.

ToF SIMS is used to measure surface chemistry. The method involves fires heavy, high energy ions at the surface.

As the ion collides with the surface, surface atoms are ejected. These can be detected and used to characterise the surface. Fragments with a low mass are ejected quickly from the surface whereas large fragments travel slowly. The time it takes for them to reach the detector gives us a measure of their relative mass.



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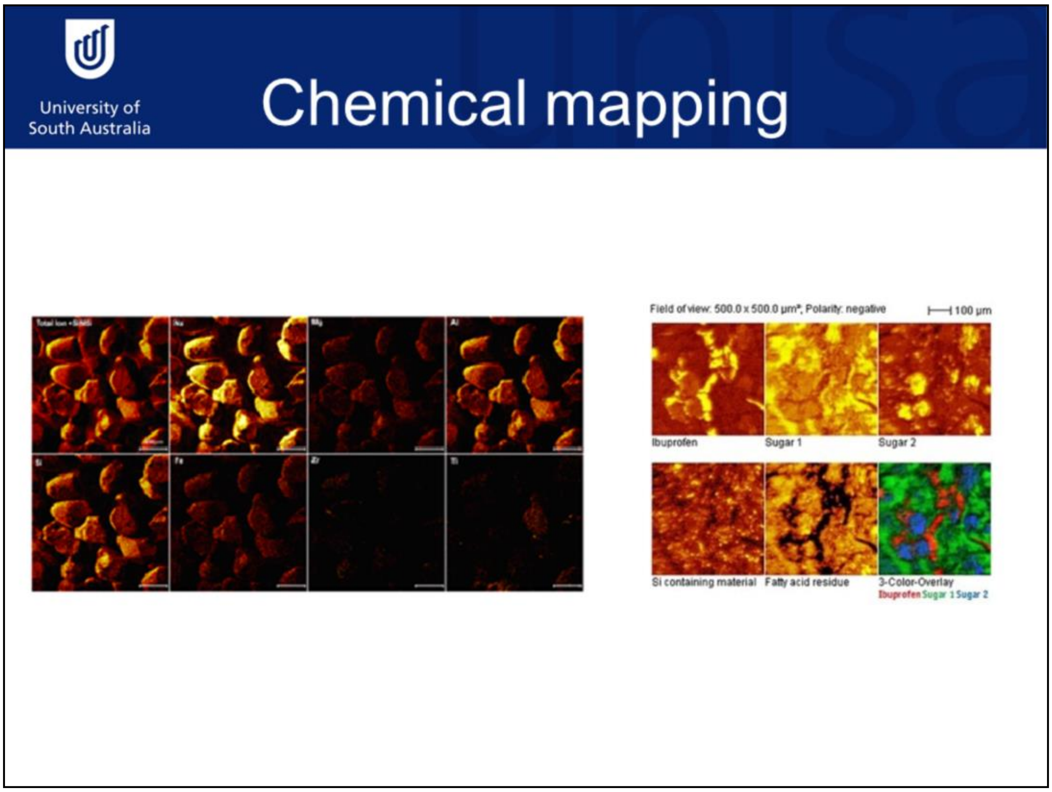
ToF-SIMS spectra

ToF-SIMS spectra of poly(ethylene terephtalate)

Here is a typical spectrum ToF SIMS spectrum. Thanks to the excellent mass resolution of these machines, each material has it's own, unique fingerprint. This spectrum is for the polymer, PET. The peaks you can see are all fragments from the surface. The downside of ToF SIMS as a technique is that it is destructive.



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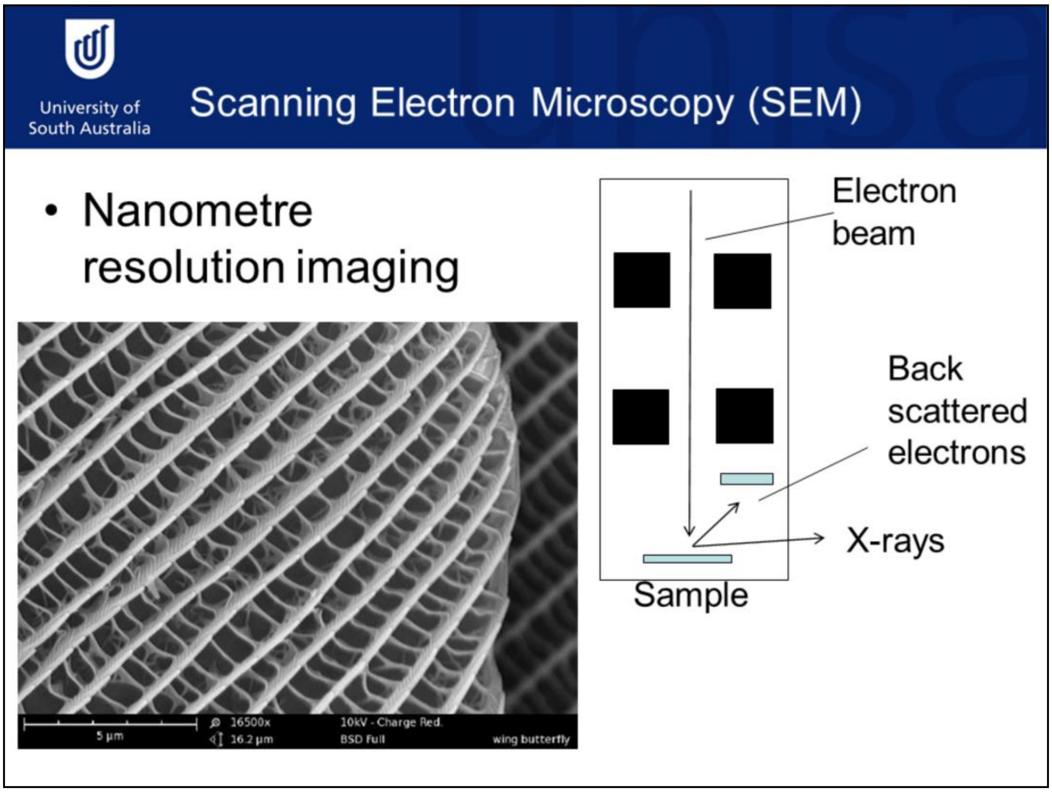
Chemical mapping

Modern Tof sims insdtruments may also be used to generate images and chemical maps of the surface. Each pixel in these images represents a complete SIMS spectrum, and as such we can use these images to identify if certain fragments or chemical groups are in particular locations on surface.



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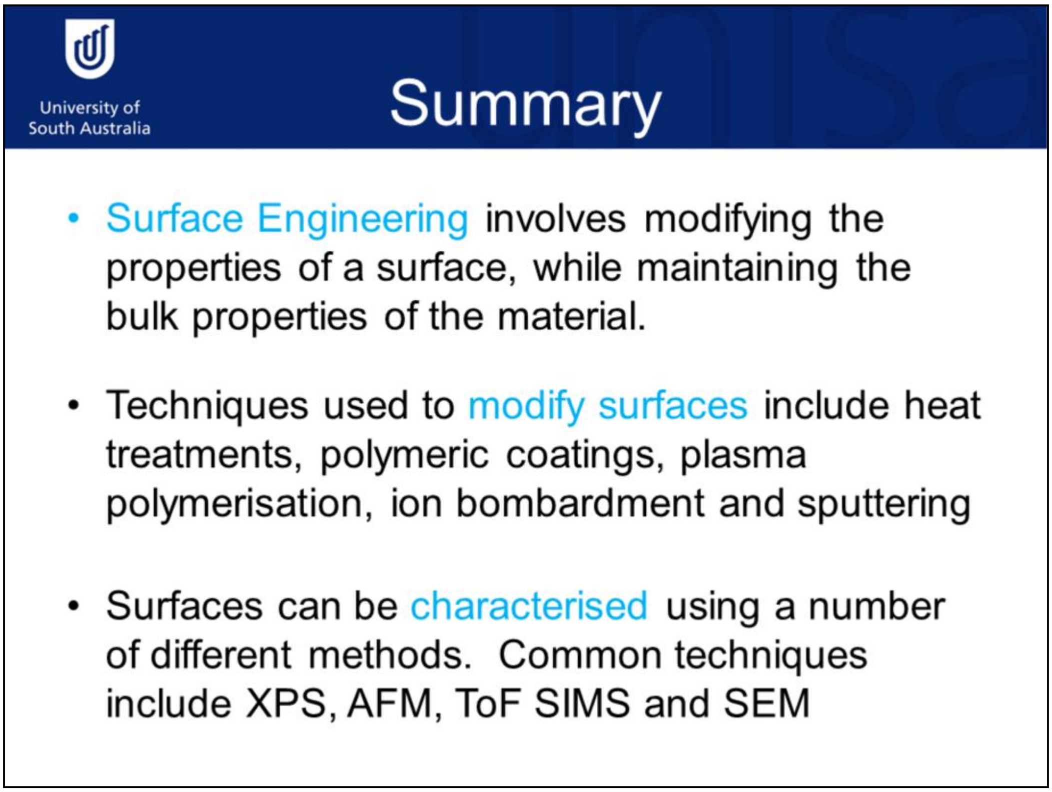
Scanning Electron Microscopy (SEM)

- Nanometre resolution imaging

The last technique we will consider is scanning electron microscopy, or SEM. Like all forms of microscopy, in SEM we look at radiation from the surface, but in this case we use an electron beam rather than light. Here an electron beam is passed through magnets in order to direct the beam, it hits the surface and is subsequently back scattered. We detect these secondary electrons and use then to build up very high resolution images. The picture here is of a butterfly wing. As the electrons are scattered, x rays are generated and these may also be collected and used to identify which elements are present.



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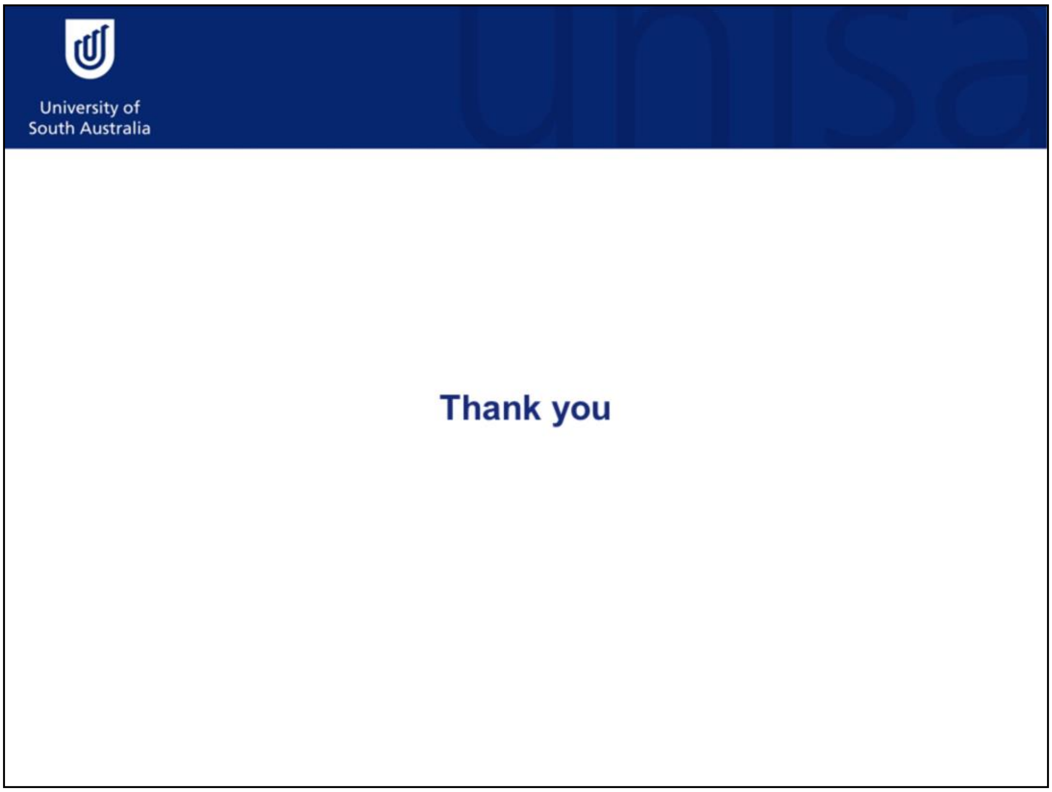
Summary

- Surface Engineering involves modifying the properties of a surface, while maintaining the bulk properties of the material.
- Techniques used to modify surfaces include heat treatments, polymeric coatings, plasma polymerisation, ion bombardment and sputtering
- Surfaces can be characterised using a number of different methods. Common techniques include XPS, AFM, ToF SIMS and SEM



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Thank you

If you have any questions or desire further clarification please post a question or comment on the Engineering Materials Discussion Forum.