Moodle Book for NS-1

This Moodle book covers the core material for NS-1. Note that the quizzes below are indexed by chapters of this book, **not** of *Modern Techniques of Surface Science*. I recommend doing each quiz straight after the Moodle book chapter and associated reading.

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1. Introduction

The **NS-1** module covers aspects of nanoscale physics, focusing on **surface science**. You may well have covered some of this material in undergraduate condensed matter physics courses. As a prerequisite you should have some knowledge of crystallography, electronic band structure (metals, insulators, semiconductors) and basic atomic physics.

- You can complete the module entirely online, at any time.
- To register, use the standard form.
- Assessment is via online problems plus a short portfolio.
- Teaching is via guided reading from the module text book and some supplementary notes.
- You need to view the online material via Moodle.
- The text book is *Modern Techniques of Surface Science,* Third Edition (D.P. Woodruff).
  ISBN 978-1-107-02310-9

Reading from this book will appear in pink bold, e.g.

Reading: section 6.1.3 HREELS   (don't read this now - HREELS is a wonderful technique but we won't cover it)

The aim is to introduce you to some key aspects of surface science, from an experimentalist's perspective. We will cover the following topics:

- Surface crystallography and surface reconstruction
- An overview of surface structure determination methods
- Surface and thin film diffraction (electrons and X-rays)
- X-ray photoemission spectroscopy (XPS) and other electron spectroscopies

I will show some scanning tunnelling microscopy (**STM**) and atomic force microscopy (**AFM**) images. But we do NOT cover these techniques in the course, and we won't interpret these images in any detail. All I will say about STM in the context of this module is: *beware, we are not "seeing atoms"!*

2. Surfaces

2.1. What is a surface?

Atoms in a bulk material exist in a certain local environment defined by their neighbours. In a perfect crystal this local environment is very well defined. In amorphous materials such an environment can be understood statistically. But in all cases, atoms at a surface clearly have a different local environment - they are missing their neighbours over roughly half of their surrounding solid angle. One might therefore simply define a surface as *the layer(s) of atoms lacking the bulk bonding environment*. But this definition fails to encapsulate any "knock-on" effects of changes of atomic bonding in the outermost layers which may propagate down several atomic layers, nor the possibility that the surface might have longer-range **electronic** effects, nor the possibility that the chemical structure of a compound material might be altered close to a surface.

Read this PDF about the different length scales for these surface effects. In the equation for Thomas-Fermi screening length the parameter a_0 is the Bohr radius, which can be modified by the electron effective mass m^* and the static dielectric constant $\varepsilon_{(0)}$ of the material.

Modern Techniques of Surface Science introduces the terminology "selvedge" (see Fig. 1.8, p. 25-26) but this is no longer common usage in my view. The idea that different depths below the outermost layer of atoms can change electronically, structurally or chemically compared to the true bulk is very important, whatever nomenclature one chooses to use.

We may study surfaces for a variety of reasons. Nanomaterials and 2D materials inherently have high surface-to-bulk ratio (2D materials can in a sense be considered "all surface"). Catalysis depends on surface chemical reactions. Thin film growth, e.g. by molecular beam epitaxy (MBE), relies on surface behaviour - wetting, surface diffusion, etc. Many electron spectroscopy techniques (e.g. X-ray photoelectron spectroscopy, XPS) are inherently surface-sensitive and so even if the surface is not of primary interest, with such a method it cannot be ignored. Semiconductor heterostructures and devices are critically dependent on surface and interface effects. **Think about how your PhD problems / materials / experiments relate to surface effects - this will be a portfolio question later on.**

Reading: section 1.1 "Why Surfaces?"

2.2. Clean surfaces and the importance of vacuum

We will consider atomically clean surfaces in ultra-high vacuum (UHV) in this module. This allows for characterisation of very well defined surfaces. UHV is usually required to maintain atomically clean surfaces for a long enough period to do experiments before they are contaminated by gas molecules arriving and sticking via dispersion forces (physisorption) or chemical bonds (chemisorption).

Reading: sections 1.2 "UHV, contamination and cleaning" and 1.3 "Adsorption"

If you want to learn more about how to achieve and maintain UHV, you should take the Vacuum Science module.

Note that *ex vacuo* chemical cleaning can be quite effective in preparing some surfaces (Woodruff mentions only *in vacuo* chemical cleaning via gas processing in the vacuum chamber). For example, wet chemical etching of GaAs using an HCl : isopropanol mixture can strip away the native Ga-rich oxides and leave the surface terminated with a passivating layer which can prevent re-oxidation for long enough to get the surface into vacuum, whereupon annealing can remove the passivating layer to reveal a reasonably clean surface. Such wet etching procedures can reduce preparation times and improve workflow for many experiments.

Another example of a surface which is highly resistant to atmospheric contamination is graphene grown on copper, which is usually produced by chemical vapour deposition (CVD). Such samples can be transferred to UHV through air without acquiring a significant coverage of chemisorbed species. A short anneal in UHV to remove physisorbed contamination can produce an atomically clean graphene / Cu surface. (Note that a graphene coating can actually make *long-term* corrosion of metals worse!)

Woodruff discusses the terminology used for quantifying exposure of a surface to gas atoms, in particular the Langmuir unit 1 L = 10^{-6} torr s. It is also worth noting that the word "monolayer" is frequently employed in surface science and MBE growth, but this is also not always clearly defined in terms of a number of atoms per unit area. The best approach is to be internally consistent (define your terms quantitatively in a given paper, report or chapter) and recognise that quantitative discrepancies with the published literature may arise.

2.3. Crystal surfaces

We will deal with crystalline surfaces in this module. **Make sure you are happy with your bulk crystallography before continuing:** Miller indices, symmetries, bracket conventions {} () [] <>, etc. For example, can you sketch for a face-centred cubic structure the (100), (110) and (111) planes and identify their in-plane symmetries? Can you draw the (0001) plane of a hexagonal structure with the principal in-plane directions of type <1-100> and <-2110>? Can you sketch the (210) plane of a simple cubic structure and calculate its angle to the (100) plane? Remind yourself of the Ewald sphere construction for reciprocal space and diffraction.

Reading: sections 1.6 "Surface Symmetry" and 1.7 "Overlayer structure"

Now have a look at this PDF on non-ideal surfaces. Real surfaces are not infinite planes of nicely arranged atoms...

2.4. Surface reconstruction

We need to distinguish *surface relaxation* from *surface reconstruction*. In section 2.1 I showed you some changes of electron density near a metal surface and some changes of atomic plane position in MnSb perpendicular to the surface. Changes of this nature - out-of-plane only - are known as surface relaxations. They are common in metals due to the local changes of electron density and packing density around atoms near the surface. Surface stress also plays a role in surface relaxation of metals. Metals usually lack directional bonds and so there is not a strong driving force for surface reconstruction, in which the periodicity of the surface unit mesh is larger than that of the terminated bulk unit cell.

Have a look at these two pages on reconstruction in **metals** and **ionic solids**.

In the case of materials with strong directional bonds - principally covalently bonded solids - we need to worry about how these bonds "see" the termination of the crystal. The energy costs of stretching or compressing such bonds are typically high, and the energy costs of partially unfilled bonds sticking out into the vacuum, so-called dangling bonds, are also high. These materials normally show strong surface reconstruction. We will look in detail at III-V semiconductors.

2.5. Case study: III-V semiconductors

The III-V semiconductors are of major importance in optoelectronic devices (sensors, LEDs, laser diodes, etc.). They have a range of surface reconstructions, some quite complex, which can affect interface formation in MBE growth, and their surfaces have been studied for several decades. Materials include InSb, GaAs, InP, GaN, etc. while alloys such as (In,Ga)As and (Al,Ga)As are critically important for band-gap engineering. We will consider GaAs, which has been widely studied. You already saw some STM images of two vicinal GaAs surfaces (section 2.3) and these showed strong "stripes" due to the (2×4) reconstruction.

Read these notes on III-V reconstructions and the **electron counting rule**.

Note that group IV semiconductors like Si also have strong covalent bonds and hence surface dangling bonds. Their reconstructions can be simpler because all the atoms have equal valence charge, e.g. dimers on (001) forming a (2×1) rather than the (2×n) necessary for charge neutrality on a III-V. However, the famous Si(111)-(7×7) dimer-adatom-stacking fault reconstruction is rather complicated, needing more than just dangling bond minimisation to explain.

Now try the Chapter 2 Quiz.

3. Electron diffraction

3.1. Background

In this chapter we will cover the basics of low energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED). LEED is most commonly used in surface science experiments as a primary characterisation tool, usually supporting other experimental techniques, while RHEED is most commonly used during thin film epitaxial growth in UHV. The main UHV expitaxial growth technique is molecular beam epitaxy (MBE) but pulsed laser deposition (PLD) can also be done in UHV and analysed by RHEED.

It is important to understand why electron diffraction is well suited to surface study. Typical X-rays (energies keV to tens of keV) interact much more weakly with solids that do electrons (energies tens of eV to tens of keV). It is difficult to achieve sufficient scattered intensity from the small number of atoms at a surface using X-rays which makes measurements in the laboratory essentially impossible. However, synchrotron radiation sources provide enormously brighter X-ray beams than lab sources and surface X-ray diffraction (SXRD) becomes possible using such sources. Beamline I07 at Diamond Light Source is the main SXRD facility for the UK. However, electron beams have such a strong interaction with matter that they are efficiently scattered by just a few atomic layers of material. Hence LEED and RHEED provide excellent surface sensitivity and surface specificity using compact electron guns in the lab.

Reading – sections 1.4 and 1.5 (surface sensitivity/specificity and X-ray / electron sources)

3.2. Reciprocal space for surfaces

Reading – section 3.1.1 "Reciprocal net and diffraction"

Diffraction is described in reciprocal space and the Ewald sphere construction is useful to understand the process. For surfaces or 2D meshes in real space, one can imagine separating the layers of a 3D mesh to infinity such that the spacing of reciprocal net points perpendicular to the separation direction goes to zero. This forms reciprocal mesh **rods** (figure 3.1). One result of this is that all outgoing k-vectors will intersect a rod at some point.

3.3. LEED

Low energy electron diffraction provides a very convenient way to measure the periodicity of a crystalline surface.

Reading – section 3.1.2.1 Qualitative considerations for LEED

However, actually determining full structures is much more difficult since single-scattering theory does not apply to strongly-interacting low energy electrons. In the next Moodle chapter you will look at how to get actual structural data from LEED experiments.

3.4. RHEED

Reflection high energy electron diffraction only requires grazing incidence access to a sample (LEED needs more or less the whole solid angle in front of a sample) so is very convenient for samples under incident fluxes, e..g. during deposition or thin film growth. Hence it is strongly associated with in situ analysis during MBE growth.

Reading – section 3.1.3 RHEED

You should also look through these slides on RHEED by Dr. Chris Burrows, to which I have added some notes in green.

Now try the chapter 3 quiz.

4. Surface structure determination

4.1. Electron diffraction

Electron diffraction gives us a rapid, simple way to assess surface periodicity and symmetry. But it does not tell us "where the atoms are within the unit mesh" in a quantitative sense without more complicated analysis. The same strong electron-solid interaction which provides surface sensitivity and specificity also prevents simple kinematical analysis of scattered intensities. LEED can be used to measure structural parameters in a quantitative way, but multiple scattering calculations of the intensities need to be done and compared to experimental data via an "R-factor". This procedure is not trivial and accurate calculations also need inelastic scattering and finite temperature effects to be accounted for.

Reading: sections 3.1.2.2 to 3.1.2.4 on quantitative structure by LEED

4.2. Surface X-ray diffraction

Using very intense synchrotron X-ray beams at grazing incidence allows the weak scattering of X-rays (some 10^6 times smaller cross section) to be overcome and surface sensitive and specific measurements to be made. Beamline I07 at **Diamond Light Source** supports SXRD work in the UK.

Reading: section 3.1.4 on SXRD

4.3. Ion scattering

Diffraction techniques rely on a reciprocal space description of the crystal structure. Ion scattering methods are understood entirely in real space and can hence be highly complementary. The principal methods structural methods are low energy ion scattering (LEIS - normally a few keV) and medium energy ion scattering (MEIS - normally ~ 100 keV). High energy ion scattering (around 1 MeV) is commonly called Rutherford Back-Scattering (RBS) and is used for depth-profiling the chemical composition of samples, but does give information on bulk crystallinity.

In the UK, one can do MEIS work at the **UK MEIS Facility** based now in Huddersfield. The **Surrey Ion Beam Centre** provides RBS and other facilities.

Reading: section 2.4 on ion scattering spectroscopy (you can skip 2.4.2 on charge exchange effects)

These sections should have given you an insight into how ions interact with surfaces and the underlying bulk. The basic idea is that the shadow cones behind surface atoms get narrower as the ion energy increases. Ion channelling - when ions undergo many low angle collision with nuclei and travel far down into the crystal along high symmetry directions - is stronger for high energy ions. Hence RBS "looks" a long way into a sample and is sensitive to bulk crystallinity, while LEIS is very surface-specific.

The use of LEIS and MEIS for surface structure determination essentially means measuring energy and angular distributions for ions scattered with different incidence geometries. Various modelling strategies can be applied to predict these spectra, e.g. via trajectory simulation across the range of possible impact parameters. These are sensitive to atomic positions within the surface, allowing precise triangulation of surface atoms relative to the bulk.

Reading: section 3.3 on ion scattering methods for surface structure

Now try the short quiz for Ch. 4.

5. Surface chemical composition

It is not always clear what the chemical composition of a surface is. This could well differ from the bulk chemical composition due to surface reconstruction, surface segregation, unintentional contamination (e.g. native oxide) or deliberate deposition of overlayers. The primary method for obtaining surface chemical information is **X-ray photoelectron spectroscopy (XPS)**. Most universities have their own high performance XPS systems, often run as user facilities, e.g. Warwick's facility.

We looked briefly and LEIS, MEIS and RBS (ion scattering methods) for composition and crystal structure analysis but will not discuss these further, though MEIS and LEIS can be very valuable for surface-sensitive compositional analysis. The other crucial ion-beam-based method for surface composition (and depth profiling essentially via drilling holes in the sample with an ion beam) is **secondary ion mass spectrometry (SIMS).** Low ion energy "static" SIMS can be extraordinarily sensitive to surface composition.

Read this PDF from my lecture on XPS.

Reading: section 2.2 on XPS and section 5.5.1.2 on initial/final state effects.

Now complete the short XPS quiz.