Advanced Topic Option:
Thin Films, Surfaces and Epitaxy

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Advanced Topics: Thin Films, Surfaces and Epitaxy

- Lecturer: Cormac McGuinness

**Syllabus:** basic concepts of solid surfaces and interfaces, surface crystallography, surface spectroscopy, adsorption, growth energetics, epitaxy basics, epitaxy models, general thin film growth, specialist thin film growth, nanostructures.

**Learning outcome:**
On successful completion of this module, students should be able to:
- Predict the crystallography of epitaxial systems
- Make simple models of adsorption and epitaxial growth on surfaces
- Distinguish between different practical methods of thin-film growth and connect this knowledge with modern device technology

- These notes, slideshow, and screencasts (when available) will appear at: https://www.tcd.ie/Physics/people/Cormac.McGuinness/Teaching/PY4N07.php
- Suggested exercises and reading matter including book excerpts will also be on the course webpage.
- Some links to reference material, manufacturers websites and a further bibliography will be updated in due course.
Thin Films, Surfaces and Epitaxy

10 Lectures in course

1. Basic concepts
2. Surface crystallography
3. Surface spectroscopy
4. Adsorption
5. Growth energetics
6. Epitaxy basics
7. Epitaxy models
8. General thin film growth
9. Specialist thin film growth
10. Nanostructures

Lecture 1: Basic Concepts

A thin film is....?

A surface is....?

Some references:

“Surface Physics” Martin Prutton
“Surface Chemistry” Elaine McCash (online at webpage)
“Semiconductor Devices: Physics and Technology” by Sze and Lee, 3rd Ed., 2013 (online at webpage)
“Physics at Surfaces” Andrew Zangwill (Cambridge) 1988 (online at webpage)
“Materials science of thin films”, Milton Ohring (online at webpage)
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Why study Thin Films and Surfaces, as well as Epitaxy? (a.k.a. Surface Science, but not confined to surfaces)

- heterogeneous catalysis, corrosion (chemistry)
- semiconductor devices, interfaces (physics)
- thin film sensors, multilayers (esp. magnetic multilayers; GMR)
- epitaxy - growth of layers on other layers
- optical coatings
- electrodes (fuel cells; transparent electrodes)
- nanostructures (quantum)
- characterisation techniques
- rich history: photoelectric effect, electron diffraction
- continual progress in surfaces / interfaces / nanostructures
- surface science is tough! (vacuum, sensitivity!)

... a requirement for vacuum and vacuum chambers
Surface science and a need for vacuum

particle flux \( \Phi = \frac{1}{4} n \bar{v} \)

- number of molecules impinging on a surface per unit time
- \( n \) = particle density
- \( \bar{v} \) = average speed

\[ \Phi = n \int_{0}^{\theta_{\text{max}}} \int_{0}^{\pi} \cos(\theta) \sin(\theta) d\Omega \]

\[ \frac{1}{4} \left( \int_{0}^{\theta_{\text{max}}} \int_{0}^{\pi} \cos(\theta) \sin(\theta) d\Omega \right) \]

\[ \frac{1}{2} \left( \int_{0}^{\theta_{\text{max}}} \int_{0}^{\pi} \cos(\theta) \sin(\theta) d\Omega \right) \]

- \( \frac{1}{2} \) from average component of velocity perpendicular to surface from one side only

- Ideal gas \( PV = NkT \); \( n = N/V = P/kT \)
- Maxwell-Boltzmann distribution of velocities \( f(\nu) = \left( \frac{m}{2\pi kT} \right)^{3/2} 4\pi \nu^2 e^{-\frac{mv^2}{2kT}} \)
- Average speed: \( \bar{v} = \left( \frac{8kT}{\pi m} \right)^{1/2} \)

thus flux \( \Phi = P/\sqrt{2\pi mkT} = 2.64 \times 10^{22} P/\sqrt{MT} \)

\[ \Phi = P/\sqrt{2\pi mkT} = 2.64 \times 10^{22} P/\sqrt{MT} \]

- i.e. rate of arrival (cm\(^{-2}\) s\(^{-1}\)) when \( P \) (mbar), \( M \) (mol wt) and \( T \) (temp in Kelvin) dependence

- Example: \( 10^{-6} \) mbar \( O_2 \) (\( M=32 \)) at 300K, \( \Phi = 2.7 \times 10^{14} \) cm\(^{-2}\) s\(^{-1}\)
- typically, a surface has \( 10^{15} \) atoms cm\(^{-2}\) (typical crystal lattice spacings are about 0.25 to 0.35nm)

- What does flux imply: surface stays clean for only \( \sim 3 \) seconds!
- (assuming a unity sticking coefficient…..? - can estimate how long it takes the surface to be covered in one monolayer of \( O_2 \))

- typically require vacuum of \( 10^{-10} \) mbar (or better)
  - how long will a surface stay clean at this pressure?
**Surface vs Bulk**

Surface atoms do not have full complement of neighbours,

Lower coordination number means:

- differing (increased) reactivity
- different electronic structure
- different geometric structure:
  - relaxation - outer layer moves in or out
  - reconstruction - outer layer(s) adopt new geometry

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**Surface structure?**

*Surface structure to be covered in lecture 2*

- stepped/kinked surfaces serve as models for defect behaviour

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*edge atom*  
*(111 plane)*  
*(100 plane)*  
*corner atom*  

Surface energies and thermodynamics determine nanoparticle morphologies
**Characterising a surface?**

- **Surface to volume ratio:**
  cubic sample, 1 cm x 1 cm x 1 cm, will contain ~ $10^{22}$ atoms, of which ~$10^{15}$ atoms are on the surface, a ratio of 1 in $10^7$! Surface dominates the smaller one goes.

- **Surface-sensitive probes:**
  - Low energy electrons & ions
  - Energy-dependent mean free path
  - Incident and emergent

- **Optical probes not suitable unless:**
  - Photoelectron spectroscopy
  - surface X-ray diffraction (pref LEED)
  - other tricks (optical symmetry selection of surface but not bulk e.g. surface reflection anisotropy spectroscopy)

  Surface probes to be covered in lectures 2 & 3

**Forming a surface/thin film**

- **Ex vacuo:**
  - “as received”
  - degrease with solvent
  - chemical etch

- **In vacuo cleaning:**
  - Mechanical (abrasion, fracture, cleaving)
  - Thermal (desorption, dissolving into bulk)
  - Ion etch (depth profile, SIMS)
  - Chemical reaction (e.g. C on W, gas dosing)

- **In vacuo deposition:**
  - Gas adsorption (traditional surface science)
  - Evaporation (thermal, plasma etc)
  - Molecular beam epitaxy
  - Surface as substrate
  - Growth in place by diffusion (e.g. graphene layer on SiC diffusing out of bulk)

- Patterning - nanostructures - separate from surface prep.
Surface as substrate

- Thin films are not self-supporting

- Surface becomes a substrate
  - Usually flat, clean
  - Inert, if no other role (but see epitaxy)

- Epitaxy:
  - Substrate crystallinity ‘seeds’ the thin film crystallinity
    - See lectures 6 & 7

- Deposition: See lectures 8 & 9

Deposition

Evaporation in ultra high vacuum (UHV)

Deposit a thin film on a clean surface

Epitaxial growth if conditions, growth energetics allow for this.

See lectures 8 & 9
### Three thin film GROWTH MODES

**Franck-van der Merwe (FM)**  
layer-by-layer growth

**Stranski-Krastanov (SK)**  
initially layer-by-layer  
then 3D islands on top

**Volmer-Weber (VW)**  
3D islands from the start  
(plus further variations)

**Increasing deposition / amount of material**

**Energetics of growth:** See lecture 5
Thin films and surfaces at work!

- Why high-\(k\) material for gate oxide? Think capacitor, same \(C\) for larger \(d\) (hence, less tunnel-leakage)
- But introduces two further problems (with solutions):
  - (1) gate/dielectric interface roughness (use ALD)
  - (2) screening by gate material (replace polysilicon with metal)
- See "The High K Solution" online with lecture notes

Other applications - see lecture 10

Devices - epitaxy of multiple layers; superlattices

- III-V solar cells; III-V quantum wells; LEDs and lasers; communications
- Multiple interfaces involving epitaxy

Other applications - see lecture 10

MBE / epitaxy basics of III-Vs + novel systems see Lectures 8, 9 and 10
New realm of interfacial electronics - atomic level control

- Oxide electronics and interfaces - a new world order
  - Solar cells; water splitting; LEDs and lasers; multiferroics and magnetic functionalities; magnetoelectronics; superlattices; superconductors; spintronics; 2D electron-gases trapped at interfaces; topological physics; fundamental physics; see e.g. "Oxide and interfacial electronics: The 2016 oxide electronic materials and oxide interfaces roadmap", M Lorenz et al 2016 J. Phys. D: Appl. Phys. 49 433001.
  - Other applications - see lecture 10

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