Lecture 2

Surface Structure

Quantitative Description of Surface Structure
- clean metal surfaces
- adsorbed covered and reconstructed surfaces
- electronic and geometrical structure

References:
1) Zangwill, p.28-32
2) Woodruff & Delchar, Chapter 2
3) Kolasinski, Chapter 1
4) Luth, 78-94
5) Attard & Barnes, 17-22

Basics: Clean Surfaces and Adsorption

1. The atom density in a solid surface is \( \sim 10^{15} \text{ cm}^{-2} (10^{19} \text{ m}^{-2}) \)
2. Hertz-Knudsen equation

\[
Z_w = \frac{p}{(2\pi nkT)^{1/2}}
\]

\( \Rightarrow \) If the probability that a molecule stays on the surface after it strikes it \( = 1 \)
(sticking coefficient \( = 1 \)),
- at \( p = 10^{-6} \text{ Torr} \) it takes \( \sim 1 \text{ s} \) to one molecule thick layer (1 ML)
- at \( p = 10^{-10} \text{ Torr} \) it takes \( \sim 10^{4} \text{ s} = 2.75 \text{ hrs} \) for 1 ML

When molecule adsorb via chemical interaction, they stick to well-defined sites

\( \Rightarrow \) Need to understand the structure of clean and adsobate-covered surfaces
as a foundation for understanding surface chemical problems
2.1 Bulk Truncation Structure

**Ideal flat surface**: truncating the bulk structure of a perfect crystal

Miller Indices, revisited
- For plane with intersections at $b_x$, $b_y$, $b_z$
  write reciprocals: $\left[ \frac{1}{b_x}, \frac{1}{b_y}, \frac{1}{b_z} \right]$

- If all quotients are rational integers or 0, this is **Miller index**
  e.g., $b_x, b_y, b_z = 1, 1, 0.5 \implies (112)$

- In general
  Miller index $(i, j, k) = \left( \frac{cd}{b_x}, \frac{cd}{b_y}, \frac{cd}{b_z} \right)$ where $cd$ - common denom. of $b_x, b_y, b_z$.

  e.g., $cd = 12; (i, j, k) = \left( \frac{12}{2}, \frac{12}{3}, \frac{12}{4} \right) = (643)$: plane 2

Crystallographic planes

- **Single plane** $(h \ k \ l)$

- **Notation**: planes of a family $\{h \ k \ l\}$
  $(100); (010); (001); \ldots \implies \{100\}$ are all equivalent

- **Only for cubic systems**: the direction indices of a direction perpendicular to a crystal plane have the same Miller indices as a plane

- **Interplanar spacing** $d_{hkl}$:
  \[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]
Metallic crystal structures (will talk about metal oxides later)

- >90% of elemental metals crystallize upon solidification into 3 densely packed crystal structures:
  - Body-centered cubic (bcc) ex.: Fe, W, Cr
  - Face-centered cubic (fcc) ex.: Cu, Ag, Au
  - Hexagonal close-packed (hcp) ex.: Zr, Ti, Zn

Very different surfaces!!!

fcc crystallographic planes

Cu (100)
Lecture 2: Surface Structure

**fcc crystallographic planes**

Cu (110)

Anisotropy of properties in two directions

Lecture 2

**fcc crystallographic planes**

Cu (111)

3 fold symmetry

Lecture 2
Atomic Packing in Different Planes

- **bcc** (100)
- **fcc** (100)

Very rough: fcc (210) and bcc(111)

 Bulk Truncated Structures

- fcc(100)
- fcc(110)
- fcc(111)
- bcc(100)
- bcc(110)
- bcc(111)
- hcp(100)
- hcp(110)
- hcp(111)
Cubic System

(i j k) defines plane
[i j k] is a vector ⊥ to plane, defining direction

Cross product of two vectors in a plane defines direction perpendicular to plane

\[ [i j k] = [l m n] \times [o p q] \]

Angle between two planes (directions):

\[
\cos \Theta = \frac{[ijk] \cdot [bnm]}{\sqrt{i^2 + j^2 + k^2 \sqrt{l^2 + m^2 + n^2}}}
\]

e.g., for [111], [211]

\[
\cos \Theta = \frac{2+1+1}{\sqrt{1^2 + 1^2 + 1^2 \sqrt{1^2 + 2^2 + 1^2 + 1^2}}} = \frac{4}{3\sqrt{2}} \Rightarrow \Theta = 19.47^\circ
\]

Planes in hexagonal close-packed (hcp)

4 coordinate axes (a_1, a_2, a_3, and c) of the hcp structure (instead of 3)

Miller-Bravais indices - (h k i l) – based on 4 axes coordinate system

a_1, a_2, and a_3 are 120° apart: h k i
c axis is 90°: l

3 indices (rarely used):

h + k = - l

(h k i l) \Rightarrow (h k l)
Basal and Prizm Planes

Basal planes:
\[ a_1 = \infty; \ a_2 = \infty; \ a_3 = \infty; \ c = 1 \]
\[ \Rightarrow (0\ 0\ 0\ 1) \]

Prizm planes: ABCD
\[ a_1 = +1; \ a_2 = \infty; \ a_3 = -1; \ c = \infty \]
\[ \Rightarrow (1\ 0\ -1\ 0) \]

Comparison of Crystal Structures

FCC and HCP metal crystal structures

- (111) planes of fcc have the same arrangement as (0001) plane of hcp crystal
- 3D structures are not identical: stacking has to be considered
FCC and HCP crystal structures

**FCC**
- B plane placed in a voids of plane A
- Next plane placed in a voids of plane B, making a new C plane
- Stacking: ABCABC…

**HCP**
- B plane placed in a voids of plane A
- Next plane placed in a voids of plane B, making a new A plane
- Stacking: ABAB…

Diamond, Si and Ge surfaces

(100) (110) (111)
Beyond Metals: polar termination

Zincblend structure
Note that polar terminations are not equivalent for (100) and (111)

ZnS (100)

ZnS (111)

Stereographic Projections

Project normals onto planar surface

Normals to planes

Figure 3.12 Stereographic projections on (100) showing the mirror zones relevant to polarized X-ray, X-ray, and single-crystal crystallographic. Note that right-handed axes are used, the direction of the bond propagates along [100] and [110] according to the symmetry-hand conventions of [100]. Reproduced from S. Kolasinski (1997).
2.2 Relaxations and Reconstructions

Often surface termination is not bulk-like. There are atom shifts \( \perp \) or \( \parallel \) to surface. These surface region extends several atom layer deep.

**Rationale for metals:** Smoluchowski smoothing of surface electron charge; dipole formation.

![Diagram showing surface and bulk atoms](image)

<table>
<thead>
<tr>
<th>Surface</th>
<th>(d_{123}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(110)</td>
<td>-8</td>
</tr>
<tr>
<td>Al(110)</td>
<td>-10</td>
</tr>
<tr>
<td>Au(100)</td>
<td>0</td>
</tr>
<tr>
<td>Cu(110)</td>
<td>-10</td>
</tr>
<tr>
<td>Cu(310)</td>
<td>-5</td>
</tr>
<tr>
<td>Mo(100)</td>
<td>-12.5</td>
</tr>
</tbody>
</table>

**Reconstructions**

**Rationale for semiconductors:** heal "dangling bonds" often lateral motion.

![Diagram showing top and side views of reconstructed surfaces](image)

Figure 2.9 - The Si(100)-1×1 reconstruction: (a) unreconstructed clean Si(100)-1×1; (b) reconstructed (clean Si(100)-2×1).
2.3 Classification of 2D periodic Structures

**Unit cell**: a convenient repeating unit of a crystal lattice; the axial lengths and axial angles are the lattice constants of the unit cell.

**Wigner–Seitz cell**: place the symmetry centre in the centre of the cell; draw the perpendicular bisector planes of the translation vectors from the chosen centre to the nearest equivalent lattice site. The unit cell is not unique!

**2D Periodic Structures**

Propagate lattice: \( n, m \) – integers \( \vec{T} = n\hat{a}_1 + m\hat{a}_2 \)

- Primitive unit cell: generally, smallest area, shortest lattice vectors, small number of atoms (if possible \( |a_1|=|a_2|, \alpha=60^\circ, 90^\circ, 120^\circ, 1 \) atom/per cell)

Symmetry:
- Translational symmetry \( \parallel \) to surface
- Rotational symmetry \( 1 \) (trivial), 2, 3, 4, 6
- Mirror planes
- Glide planes

All 2D structures w/1 atom/unit cell have at least one two-fold axis.
2.4 2D Substrate and Surface Structures

Considering all possibilities and redundancies for 2D periodic structures (e.g., 3-fold symmetry for $\gamma=60^\circ$, $120^\circ$, we get only 5 symmetrically different Bravais nets with 1 atom per unit cell.

When more than 1 atom/unit cell more complicated:
- 5 Bravais lattices
- 10 2D point symmetry group (cf. Woodruff)
- 17 types of surface structures

**Substrate and Overlayer Structures**
Suppose overlayer (or reconstructed surface layer) lattice different from substrate:

\[ \vec{T}_A = n\vec{a}_1 + m\vec{a}_2 \]
\[ \vec{T}_B = n\vec{b}_1 + m\vec{b}_2 \]

2.5 Wood’s notation

Simplest, most descriptive notation method (note: fails if $\alpha \neq \alpha'$ or $b/a$ irrational).

**Procedure:**
- Determine relative magnitude of $a_j, b_j$, and $a_2, b_2$
- Identify angle of rotation (here $\phi = 0$)

Notation: $R\phi$
2.6 Matrix Notation

Use matrix to transform substrate basis vectors, \( \mathbf{a}_1, \mathbf{a}_2 \), into overlayer basis vectors, \( \mathbf{b}_1, \mathbf{b}_2 \)
\[
\begin{align*}
\mathbf{b}_1 &= G_{11}\mathbf{a}_1 + G_{12}\mathbf{a}_2 \\
\mathbf{b}_2 &= G_{21}\mathbf{a}_1 + G_{22}\mathbf{a}_2
\end{align*}
\]
where: \( \mathbf{G} = \begin{bmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{bmatrix} \) so that: \( \begin{bmatrix} \mathbf{b}_1 \\ \mathbf{b}_2 \end{bmatrix} = \mathbf{G} \begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \end{bmatrix} \)

For p(2 \times 2) on cubic (100)
\[
\begin{align*}
\mathbf{b}_1 &= 2\mathbf{a}_1 + 0 \\
\mathbf{b}_2 &= 0 + 2\mathbf{a}_2
\end{align*}
\]
\[ \mathbf{G} = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix} \]

For p(2 \times 2) on fcc(111)
\[
\begin{align*}
\mathbf{b}_1 &= 2\mathbf{a}_1 + 0 \\
\mathbf{b}_2 &= 0 + 2\mathbf{a}_2
\end{align*}
\]
\[ \mathbf{G} = \begin{bmatrix} 2 & 0 \\ 0 & 2 \end{bmatrix} \]

For \((\sqrt{3} \times \sqrt{3})R30^\circ\) on fcc(111)
\[
\begin{align*}
\mathbf{b}_1 &= \mathbf{a}_1 + \mathbf{a}_2 \\
\mathbf{b}_2 &= -\mathbf{a}_1 + 2\mathbf{a}_2
\end{align*}
\]
\[ \mathbf{G} = \begin{bmatrix} 1 & 1 \\ -1 & 2 \end{bmatrix} \]

Areas: \( A = |\mathbf{a}_1 \times \mathbf{a}_2| \); \( B = |\mathbf{b}_1 \times \mathbf{b}_2| \); \( \text{det} \mathbf{G} = B / A \)

---

2.7 Comparison of Wood’s and Matrix Notation

Classification of lattices:

- Reconstruction superlattice \( b / a = 2 \)
- Adsorbate superstructures simple superlattice \( b / a = 2 \)
- Coincidence lattice \( b / a = 4 / 3 \)
- Incoherent lattice \( b / a = 1.49953 \)
Examples of Coincidence Lattice

Note that symmetry does not identify adsorption sites, only how many there are.

Domain structures:

\[(1 \times 2) = (2 \times 1)\]

Domains and domain walls

heavy wall

light wall
Consider that in the pictures you are looking down at a surface. The larger circles represent the substrate atom positions and dark dots represent the overlayer atom positions. Overlayer unit cells are shown. For each structure:

1. Draw the substrate unit cell and vectors, and the primitive overlayer unit cell and unit cell vectors.
2. Calculate the ideal coverage (in monolayers) of the overlayer.
3. If the primitive overlayer surface unit cell can be named with Wood’s notation, do so. If it cannot, try to identify a nonprimitive cell which can be so named.
4. Give the matrix notation for the primitive overlayer unit cell.
5. Classify the surface overlayer as simple, coincident or incoherent.
Try (c) and (d) at home

(c)  

(d)