Surface crystallography
Structures and notation

**What we want to know:**
- Surface unit cell (periodic structures)
- Atom positions in unit cell
- Morphology (steps, islands, domains)
- Defects

**Finally we should connect:**
- Growth <=> Structure <=> Properties

**How we can do it:**
- Real space / local probes:
  - Scanning Tunneling Microscopy (STM)
  - Atomic Force Microscopy (AFM)

- Reciprocal space / global probes:
  - Low Energy Electron Diffraction (LEED)
  - Reflectance High Energy Electron Diffraction (RHEED)
  - Grazing Incidence X-ray Diffraction (GIXD, SXRD)
Crystal lattices at surfaces

3D symmetry broken at surfaces => 14 bravais lattices in 3-Dimensions are replaced by 5 bravais lattices in 2 Dimensions

3D bravais lattices

2D Bravais Lattices

- Oblique: \( a_1 \neq a_2 \), \( \gamma = 90^\circ, 120^\circ \)
- Rectangular: \( a_1 = a_2 \), \( \gamma = 90^\circ \)
- Centered Rectangular: \( a_1 = a_2 \), \( \gamma = 90^\circ \)
- Square: \( a_1 = a_2 \), \( \gamma = 60^\circ \)
- Hexagonal: \( a_1 = a_2 \), \( \gamma = 120^\circ \)

Determination of Miller Indices (fcc)

Fig. 1.2. Examples of Miller index notation for lattice planes in a cubic system.
Different planes of fcc (faced cubic centered)

Hexagonal closed packed (hcp)

Hexagonal systems:

Ideal surfaces:

- Result from simple slice cutting a crystal in arbitrary direction
  (all atoms remain in their exact bulk positions).
- Alternative names: bulk-terminated, bulk-truncated surfaces
- Low-index: cut crystal along directions with close-packed planes,
  (100) / (110) / (111)
- High-index: all other cut directions

Four index Miller notation \( (a_1, a_2, a_3, c) \) \( n/h : n/k : n/l: n/i \)
Index \( i \) is redundant: \( n/h + n/k = -n/l \)

hcp(0001) and fcc(111) differ only in registry of third-layer
Hexagonal closed packed (hcp)

Four indices: (a) hcp(0001), (b) hcp(1010) -
Stacking sequence of hcp(0001) vs. fcc(111): AbAb… vs. ABCABC…

Common low-index planes

fcc(100)

from conventional bulk unit cell

primitive surface unit cell

FCC

BCC

(100)

(111)

(110)

(211)
Some bulk planes + surface structures

When we name bulk planes we still use (hkl):

fcc(100)  fcc(111)

Square Bravais lattices  Hexagonal Bravais lattice

Some bulk planes + surface structures

but we can now add additional structure on top (red atoms):

fcc(100)  fcc(111)

Square bravais lattices  Hexagonal bravais lattices

we must be able to classify these overlayer structures, as Bravais lattices is not enough...
Surface structure: Woods Terminology

Surface structures are described with respect to the original bulk crystal surface unit cell.

Definition of woods terminology:

Woods terminology can only be used when \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \) are rotated through the same angle \( \theta \) with respect to \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \).

A more general terminology expresses the relationship between overlayer and bulk surface as 2x2 matrices:

\[
\begin{bmatrix}
\mathbf{b}_1 \\
\mathbf{b}_2 \\
\end{bmatrix} =
\begin{bmatrix}
m_{11} & m_{12} \\
m_{21} & m_{22} \\
\end{bmatrix}
\begin{bmatrix}
\mathbf{a}_1 \\
\mathbf{a}_2 \\
\end{bmatrix}
\]

"p" or "c" denotes primitive or centered surface lattice, and \( X \) is the chemical symbol of an adsorbed species.

The substrate net is therefore denoted: "\( 1 \times 1 \)".

To understand the notation let us apply it to the structures from before...

Some bulk planes + surface structures

Naming structures with woods terminology:

f\( cc(100) \)

\[
\begin{bmatrix}
\mathbf{b}_1 \\
\mathbf{b}_2 \\
\end{bmatrix} = \begin{bmatrix}
\mathbf{a}_1 \\
\mathbf{a}_2 \\
\end{bmatrix}
\]

The structure is: p\( (2 \times 2) \)

Usually however the p will be omitted thus it will be written: \( (2 \times 2) \)
Some bulk planes + surface structures

Naming structures with Woods terminology:

- fcc(100), fcc(111), hcp(0001)
- \( (2\times2) \) \( (1\times1) \) \( c(2\times2) \) \( (2\times2) \) \( (1\times1) \) \( (\sqrt{3}\times\sqrt{3})R30^\circ \)

\[
p \left( \frac{b_1}{a_1} \times \frac{b_2}{a_2} \right) R \theta - X
\]

Simple, coincidence, incommensurate

The determinant of \( M \) can be used to characterise the relationship between the surface & substrate lattice.

\[
\det M = \det \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} = m_{11}m_{22} - m_{12}m_{21}
\]

If \( \det M \) is an integer the lattice is termed simple.
If \( \det M \) is a rational fraction the lattice is coincident.
If \( \det M \) is neither then the adsorbate lattice is incommensurate.
Examples of Wood's Notations

Masel, "Principles of Adsorption...", p.80-82

Figure C.75: Wood's notation for a number of overlayers on the (111) face of an FCC metal.

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Figure 2.73  Wood's notation for a number of overlayers on the (110) face of an FCC metal.

Masel, _Principles of Adsorption_... p.80-82
SURFACE EXPLORER Output

Selection
- Lattice type: Face centered cubic (fcc)
- Miller indices: 0 0 1
- Size: 5 x 5 x 4
- View: Perspective
- Color: Blue
- Design: Glossy balls
- Magnification: 1.20

http://w3.rz-berlin.mpg.de/~rammer/surfexp_prod/

Surface specific structures
Classification of Adsorption sites on fcc(111) or hcp(0001)

Bulk-truncated surface
Examples: in reality, none. Alkali halides come close (e.g., KF)

Relaxed surface:
in-plane structure is the same as for the bulk-truncated surface

Reconstructed surface
Examples: Au(111) Ag(110) Cu(111)

Surface relaxations and reconstructions
Dangling Bonds in Si, Ge, C, GaAs (sp$^3$ Hybrid)

Silicon (001) Reconstruction

Two neighboring surface atoms move closer to form a “dimer bond”

Each surface atom now has one dangling bond instead of two


Surface unit cell
Most prominent example:
The (7 x 7) reconstruction of the Si(111) surface

Bulk Si: diamond structure
Cut in the (111) plane

DAS (Dimer-Adatom-Stacking-fault) model

STM image

Takayanagi, Tanishiro, Takahoashi, Takahashi; Surf. Sci. 164 (1985) 367 S

Stepped surfaces

Terraces, steps and kinks resemble low-index planes

Correspondence between Miller indices and step notation not trivial!
Low miscut surfaces often called vicinal surfaces

Alternative description:
n atoms wide (hkl) terrace & (hkl) step

Classifying adsorbate sites

Adsorbate sites

On-top Bridge fcc hollow hcp hollow
Simple adsorption sites on (100), (110) and (111) - Adsorbates can form ordered overlayers, islands, domains

Coverage is often measured in monolayers

\[ 1 \text{ML} = \left( \frac{\text{#adsorbates}}{\text{primitive unit cell}} \right) = \left( \frac{\text{#adsorbates}}{\text{surface atom}} \right) \]

Different reconstructions/overlayers can lead to the same periodicity!

\[ \text{p(2x2)-O} \]
\[ \text{p(2x2)-3O} \]

N-induced clock/anticlock reconstruction

And in extreme cases: facetting...

Missing Row Reconstructions on fcc(110): O-induced reconstruction on Rh(110)

\[ \text{O}(2x1) \text{ missing row} \]
\[ \text{O}(1x2) \text{ missing row} \]

CO Adsorption on various surfaces

a)-c) fcc(111) or hcp(00001)
d)-e) fcc(100)
g) fcc(110)

CO Adsorption on Pt(110)