Surface crystallography

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)

Surface crystallography
Structures and notation

Crystal lattices at surfaces

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

3D bravais lattices

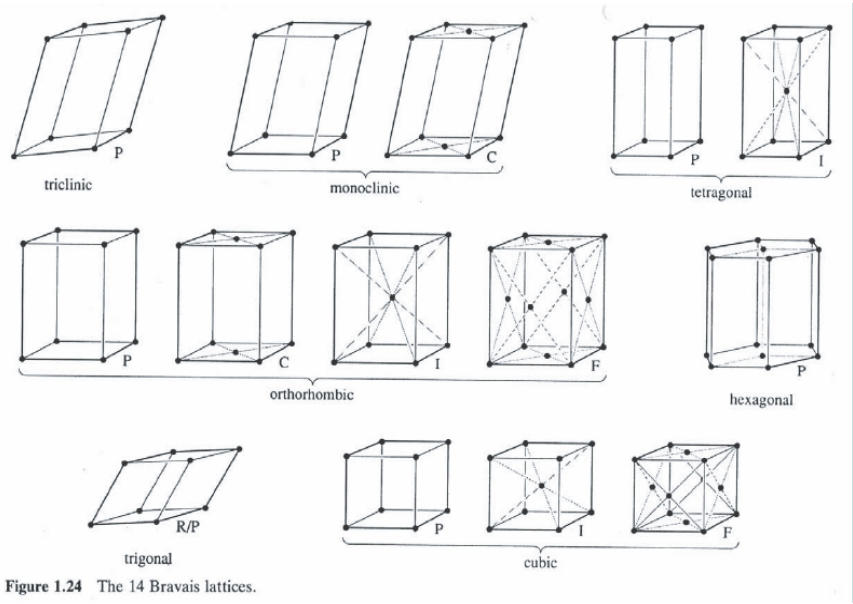
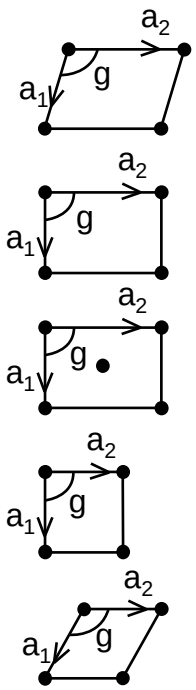


Figure 1.24 The 14 Bravais lattices.

2D Bravais lattices



oblique	$a_1 \neq a_2$	$\gamma \neq 90°, 120°$
rectangular	$a_1 \neq a_2$	$\gamma = 90°$
centered rectangular	$a_1 \neq a_2$	$\gamma = 90°$
Square	$a_1 = a_2$	$\gamma = 90°$
Hexagonal	$a_1 = a_2$	$\gamma = 120°$

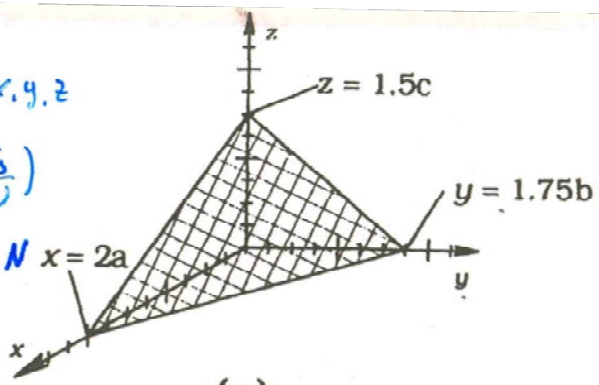
Determination of Miller Indices (fcc)

1) Achsenabschnitte bestimmen in Einheiten von $\vec{a}, \vec{b}, \vec{c}$: x, y, z

2) $\left(\frac{1}{x}, \frac{1}{y}, \frac{1}{z}\right) = \left(\frac{x_1}{N}, \frac{x_2}{N}, \frac{x_3}{N}\right)$

3) kleinstes gemeinsamer Nenner N finden

4) Miller Indizes (x_1, x_2, x_3)



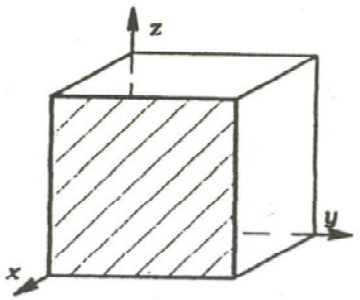
(a)

$\left(\frac{1}{x}, \frac{1}{y}, \frac{1}{z}\right)$

$= \left(\frac{1}{2}, \frac{4}{7}, \frac{2}{3}\right)$

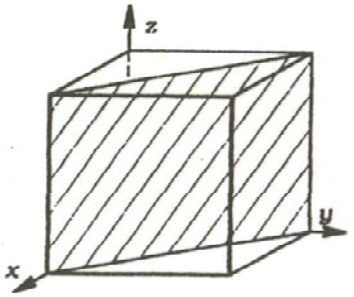
$= \left(\frac{21}{42}, \frac{24}{42}, \frac{28}{42}\right)$

$\Rightarrow (21, 24, 28)$



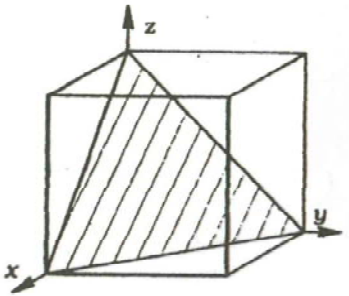
(100)

(b)



(110)

(c)

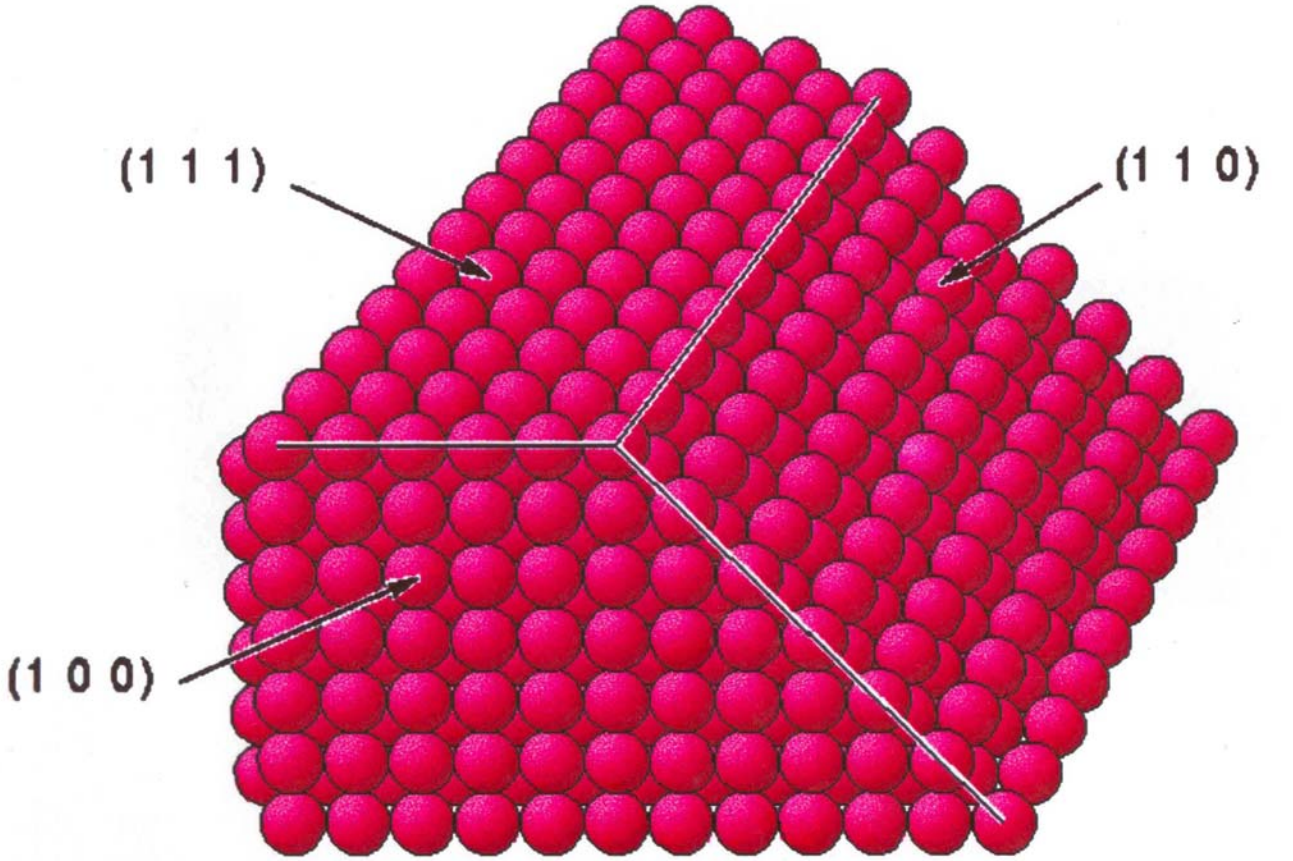


(111)

(d)

Fig. 1.2. Examples of Miller index notation for lattice planes in a cubic system.

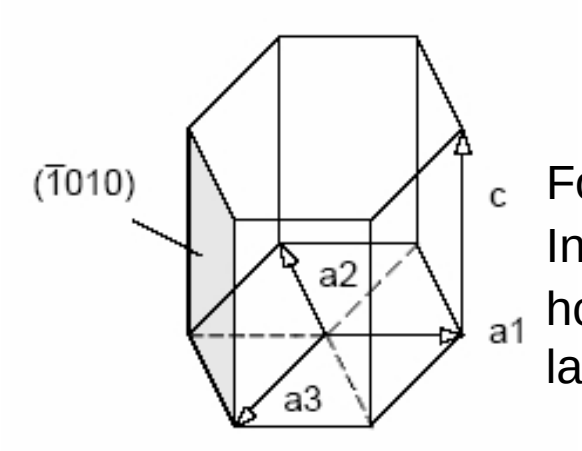
Different planes of fcc (faced cubic centered)



fcc lattice : different net planes

Hexagonal closed packed (hcp)

Hexagonal systems:



Four index Miller notation ($\boldsymbol{a_1 a_2 a_3 c}$) (*n/h : n/k : n/i: n/l*)

Index *i* is redundant: *n/h+ n/k= -n/i*

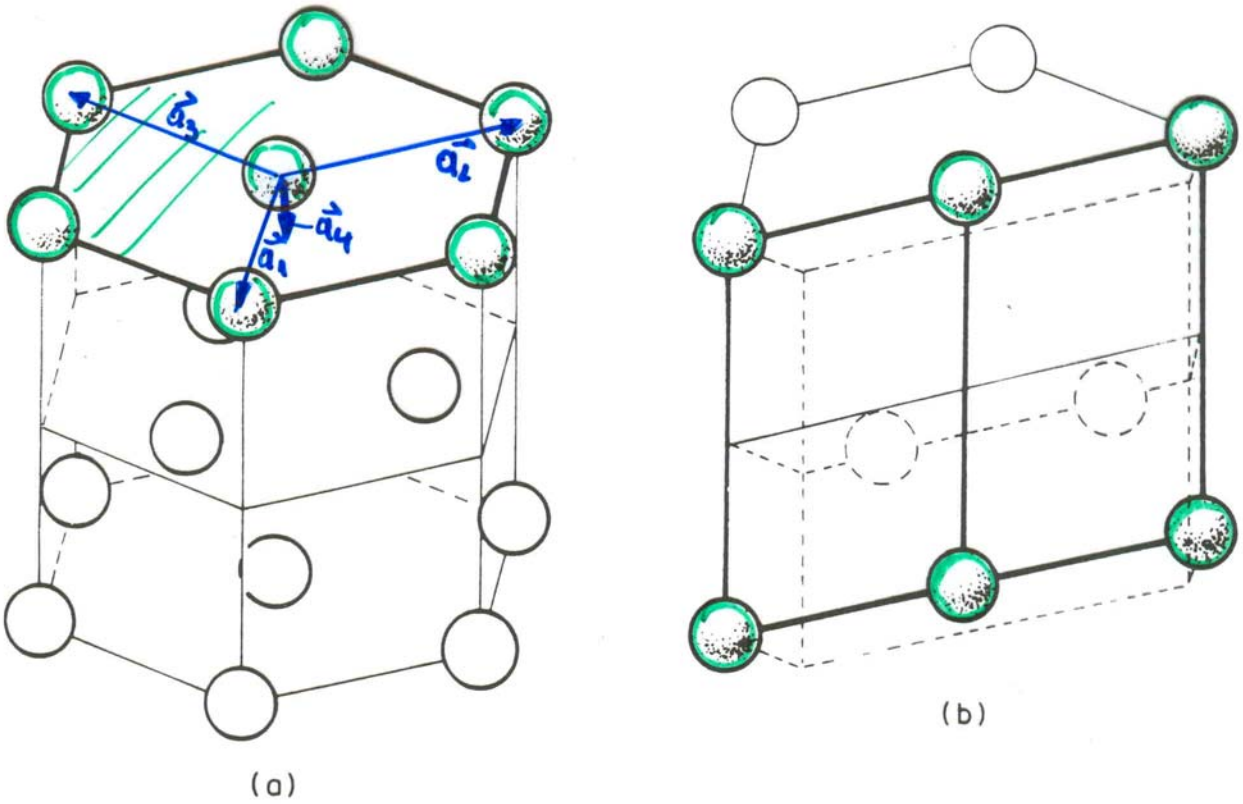
hcp(0001) and fcc(111) differ only in registry of third-layer

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

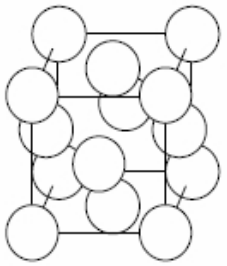
Hexagonal closed packed (hcp)

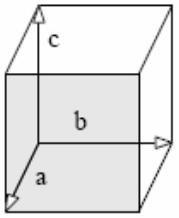


Four indices: (a) hcp(0001), (b) hcp(1010)

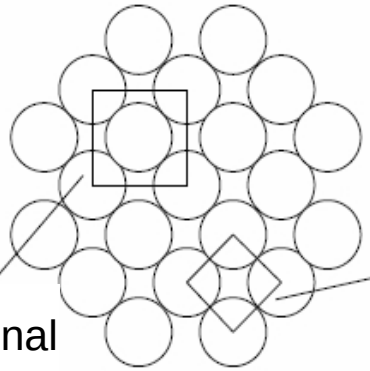
Stacking sequence of hcp(0001) vs. fcc(111): AbAb…. vs. ABCABC…

Common low-index planes



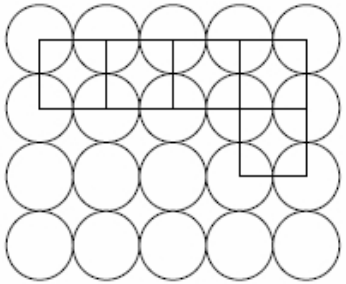


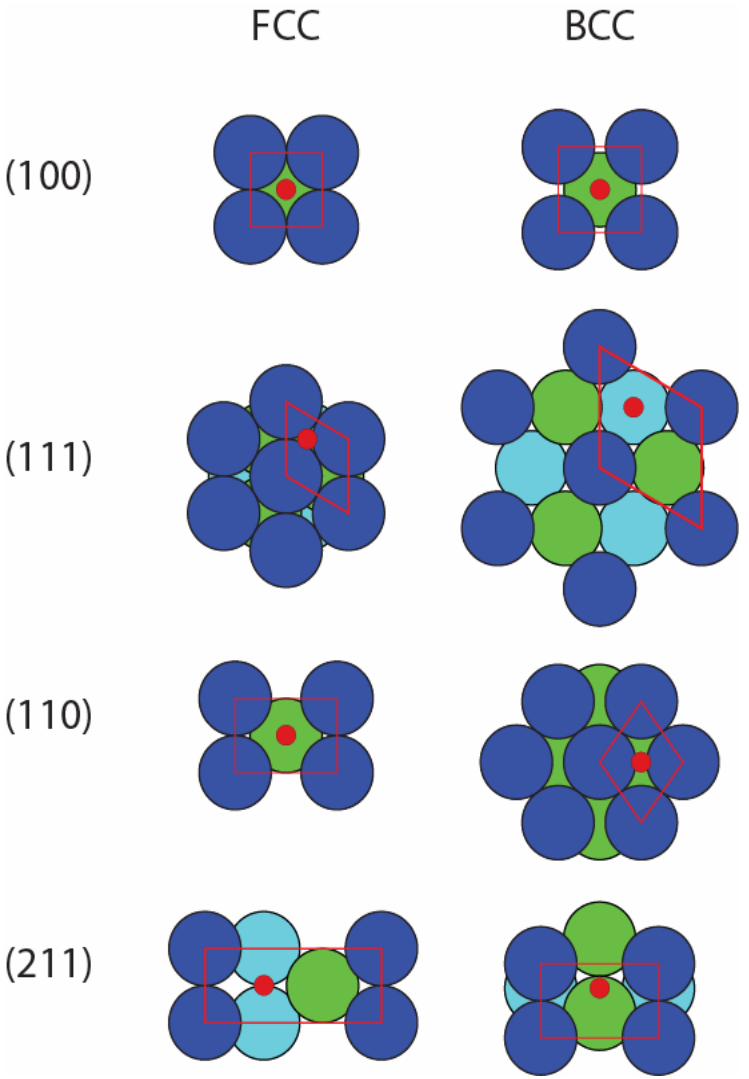
fcc(100)



from conventional bulk unit cell

primitive surface unit cell

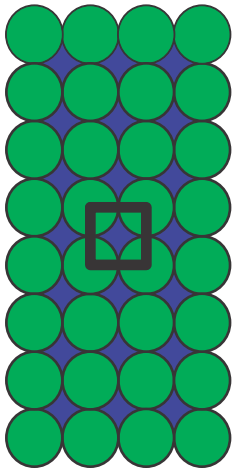




Some bulk planes + surface structures

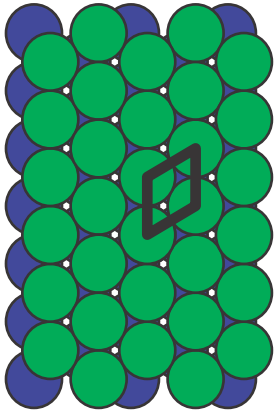
When we name bulk planes we still use (hkl):

fcc(100)



Square Bravais lattices

fcc(111)

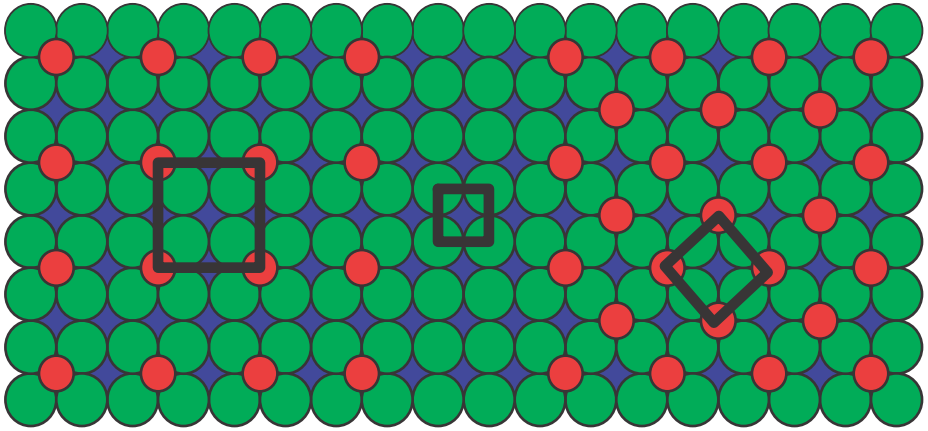


Hexagonal Bravais lattice

Some bulk planes + surface structures

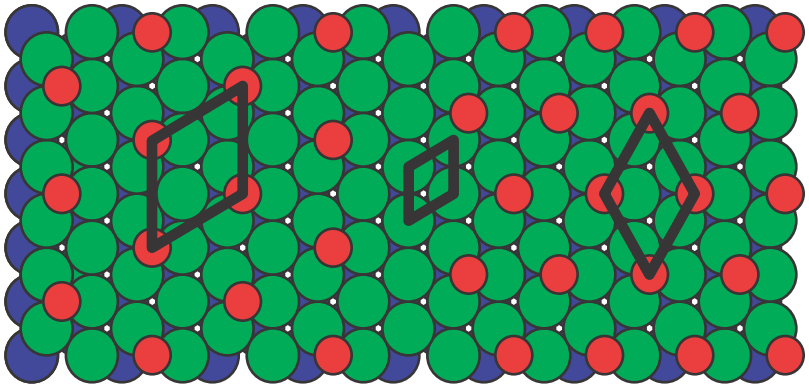
but we can now add additional structure on top (red atoms):

fcc(100)



Square bravais lattices

fcc(111)



Hexagonal bravais lattices

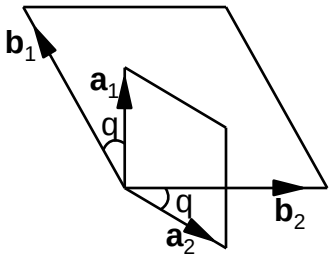
we must be able to clasify these overlayer structures, as Bravais lattices is not enough...

Surface structure: Woods Terminology

Wood, J. App. Phys. **35**, 1306 (1964) Park, Madden Surf. Sci. **11**, 188 (1968)

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

Definition of woods terminology:



$\mathbf{a}_1,\mathbf{a}_2$- vectors of bulk surface unit cell

$\mathbf{b}_1,\mathbf{b}_2$- vectors of overlayer unit cell

Structure is described as: $p\left(\frac{b_1}{a_1} \times \frac{b_2}{a_2}\right) R\theta - X$

"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 x 1)".

When it does not work:

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

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

$$\begin{matrix}\mathbf{b}_1 \\ \mathbf{b}_2\end{matrix} = \begin{matrix}m_{11}\mathbf{a}_1+m_{12}\mathbf{a}_2 \\ m_{21}\mathbf{a}_1+m_{22}\mathbf{a}_2\end{matrix} \rightarrow$$

$$\begin{pmatrix}\mathbf{b}_1 \\ \mathbf{b}_2\end{pmatrix} = \begin{pmatrix}m_{11} & m_{12} \\ m_{21} & m_{22}\end{pmatrix}\begin{pmatrix}\mathbf{a}_1 \\ \mathbf{a}_2\end{pmatrix}$$

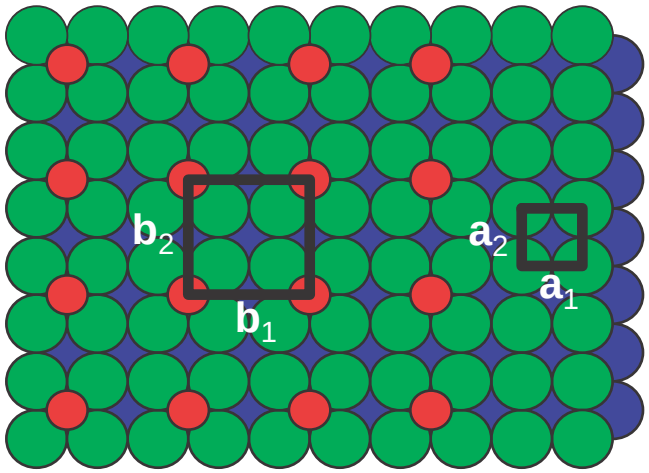
Matrix notation is VERY rarely used - often the Woods term of a overlayer with close resemblance to the probematic structure is used

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

Some bulk planes + surface structures

Naming structures with woods terminology:

fcc(100)



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

$$\theta = 0$$

$$2a_1 = b_1$$

The structure is: p(2x2)

Usually however the p will be omitted thus it will be written: (2x2)

$\mathbf{a}_1, \mathbf{a}_2$- vectors of bulk surface unit cell

$\mathbf{b}_1, \mathbf{b}_2$- vectors of overlayer unit cell

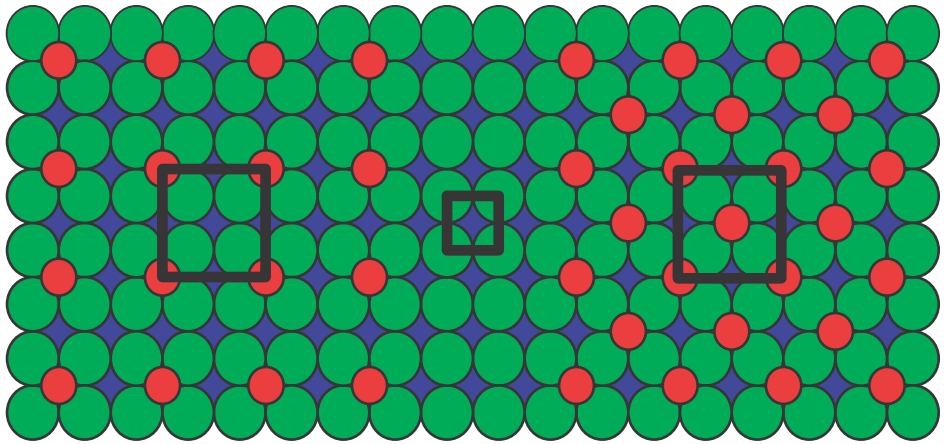
"p" or "c" denotes primitiv or centered surface lattice, and X is the chemical symbol of the adsorbed species

Some bulk planes + surface structures

Naming structures with Woods terminology:

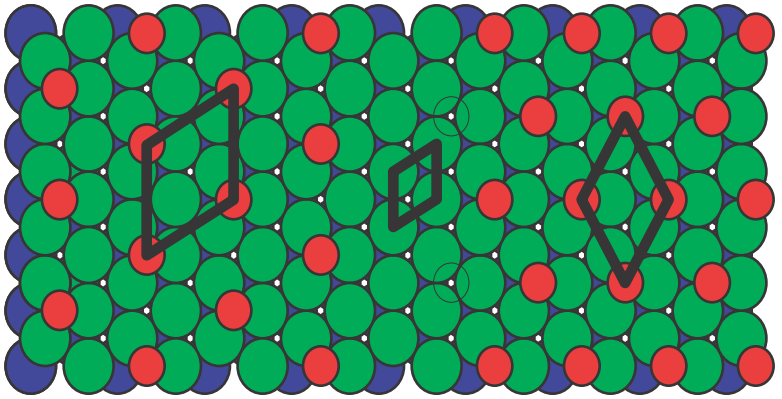
fcc(100)

(2x2) (1x1) c(2x2)



fcc(111), hcp(0001)

(2x2) (1x1) (√3x√3)R30°



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

Simple, coincidence, incommensurate

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

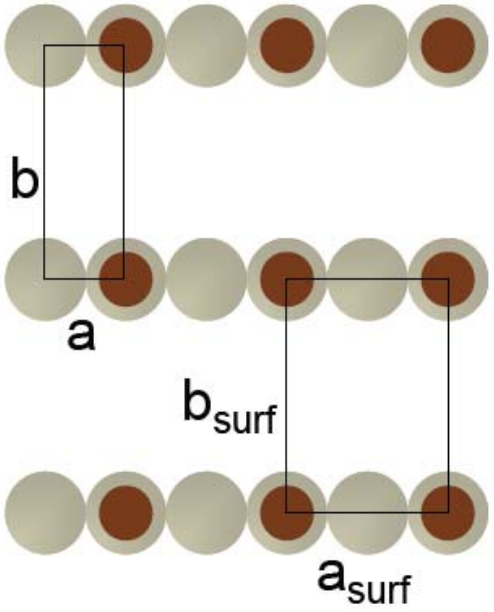
$$\det M = \det\begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} = m_{11}m_{22} - m_{12}m_{21}$$

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.

Matrix notation: *Simple*



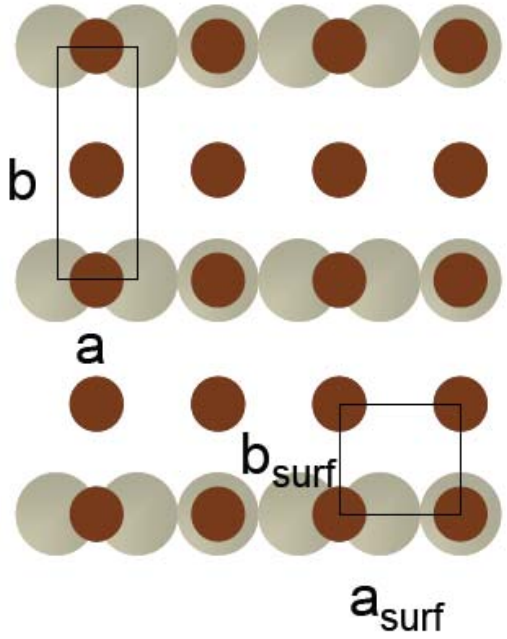
$$\mathbf{a}_{surf} = 2\mathbf{a} + 0\mathbf{b}$$

$$\mathbf{b}_{surf} = 0\mathbf{a} + 1\mathbf{b}$$

$$M = \begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix}$$

$$\det M = 2$$

Matrix notation: *Coincidence*



$$2\mathbf{a}_{surf} = 3\mathbf{a} + 0\mathbf{b}$$

$$2\mathbf{b}_{surf} = 0\mathbf{a} + 1\mathbf{b}$$

$$M = \begin{pmatrix} 3/2 & 0 \\ 0 & 1/2 \end{pmatrix}$$

$$\det M = 3/4$$

Examples of Wood's Notations

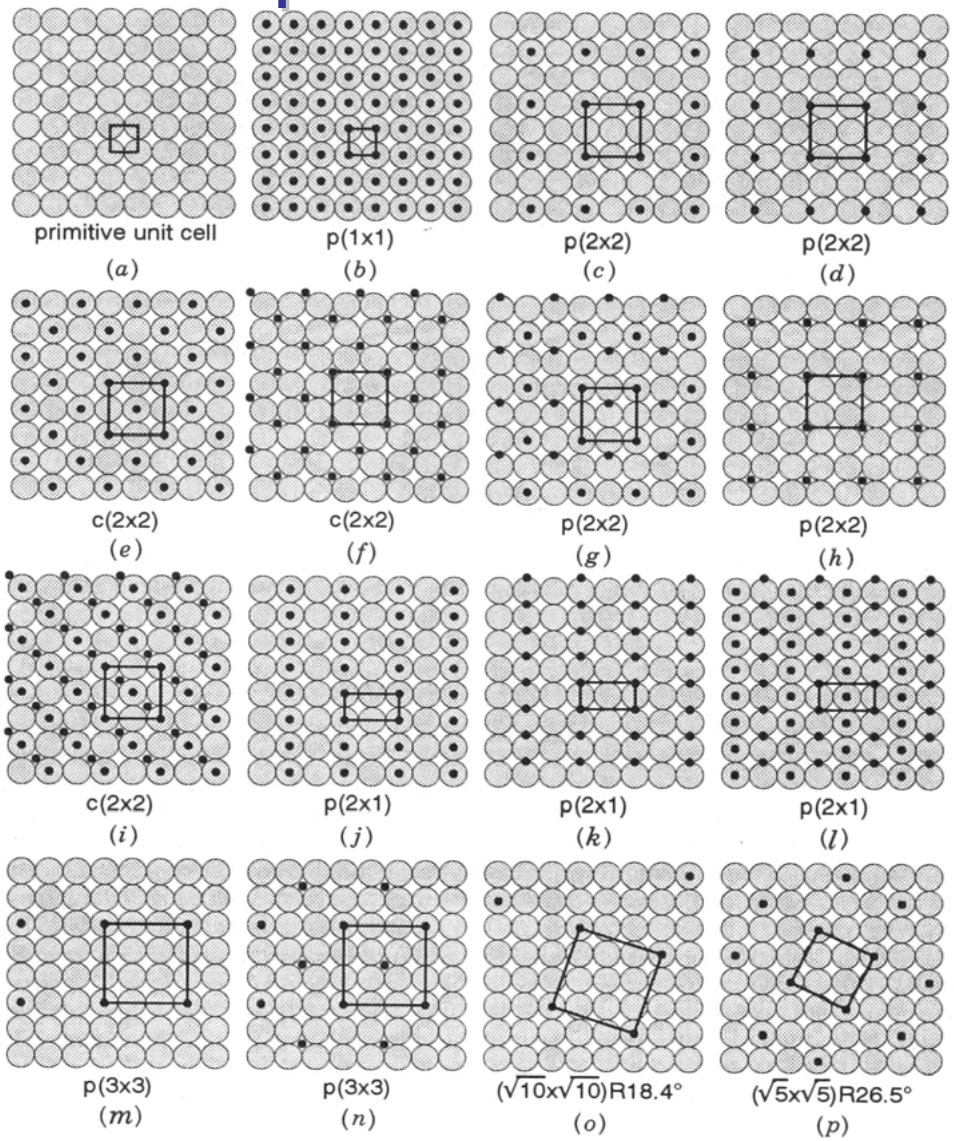


Figure 2.71 Wood's notation for a number of overlayers on the (100) face of an FCC metal.

Masel,
„Principles of Adsorption… „
p.80-82

Examples of Wood‘s Notations

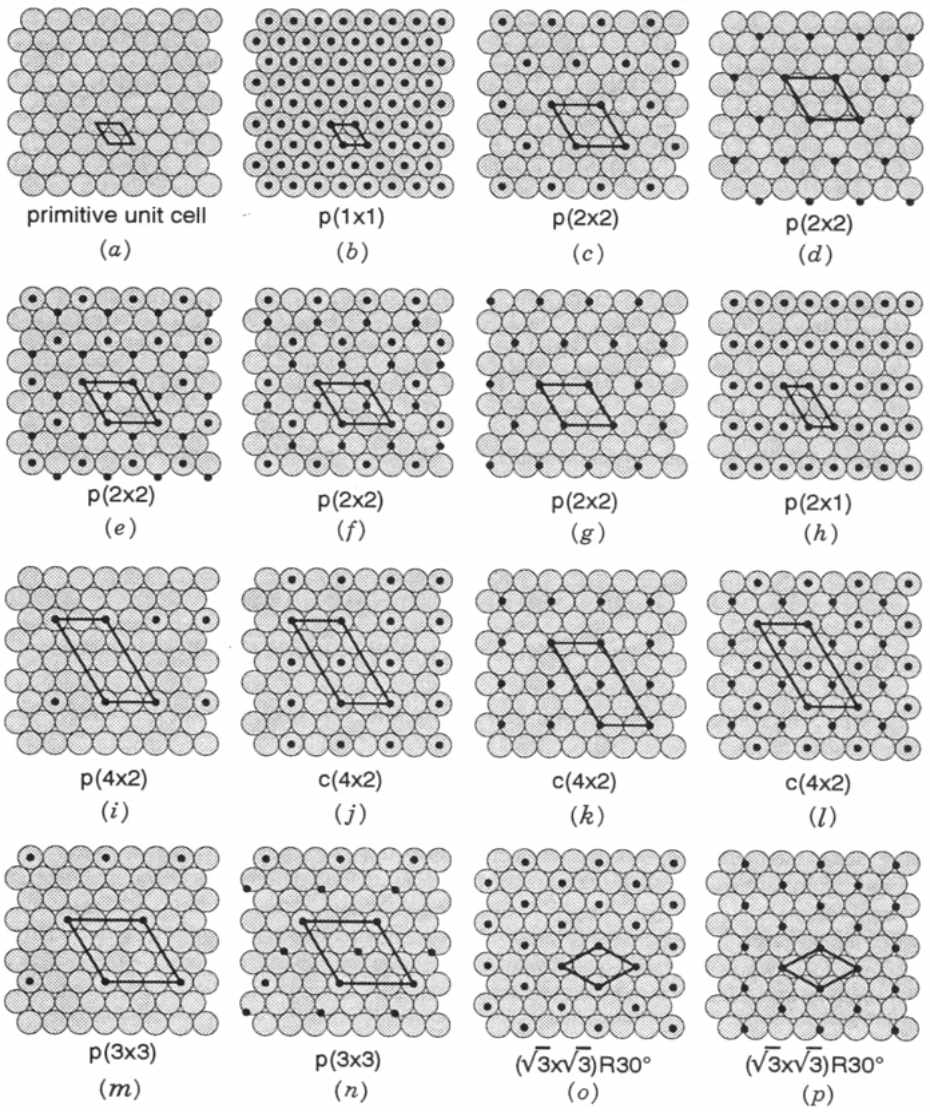


Figure 2.72 Wood's notation for a number of overlayers on the (111) face of an FCC metal.

Masel,
„Principles of Adsorption… „
p.80-82

Examples of Wood‘s Notation

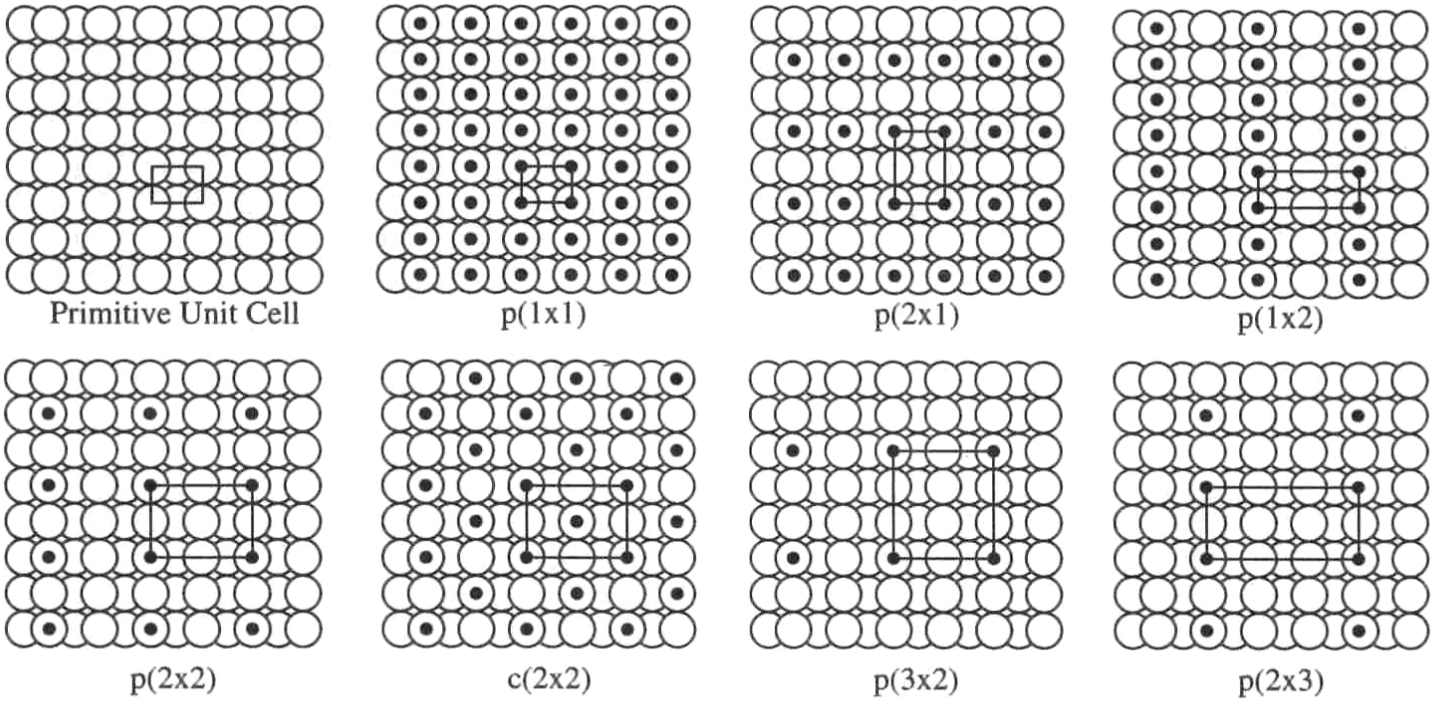


Figure 2.73 Wood’s notation for a number of overlayers on the (110) face of an FCC metal.

Masel, „Principles of Adsorption… „ p.80-82

SURFACE EXPLORER

Version 2, based on BALSAC, (C) Klaus Hermann (FHI)

Input Form :

Lattice type: Face centered cubic (fcc)

Miller indices: h 0 k 0 l 1

Size: N1 5 N2 5 N3 4 Ninit 1

View: Theta 50 Phi 10 Magnf 1.20 Perspective

Design: Glossy balls **Color:** blue Show image

VISUALIZE FORM HELP RESET FORM

For questions contact Klaus Hermann (scientific) or Fritz Rammer (technical)

Make your own surfaces...

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

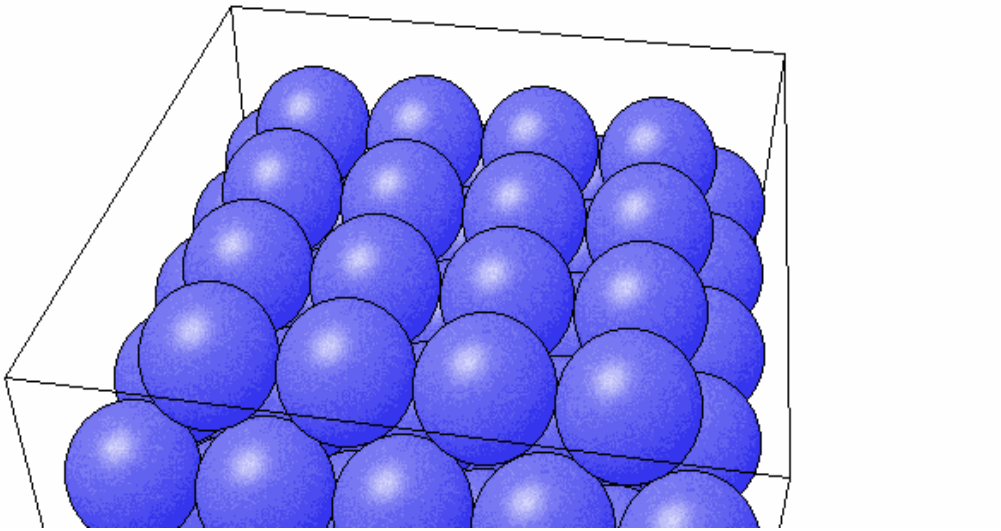
SURFACE EXPLORER

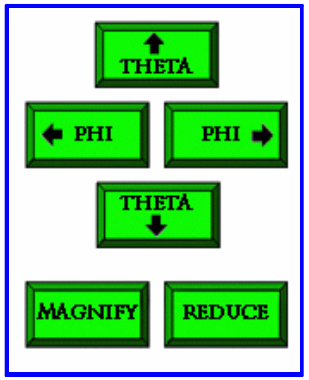
Output

Selection

Lattice type Face centered cubic (fcc)
Miller indices 0 0 1
Size 5 5 4 1
View 50 10 Perspective
Color blue
Design Glossy balls
Magnification 1.20

View



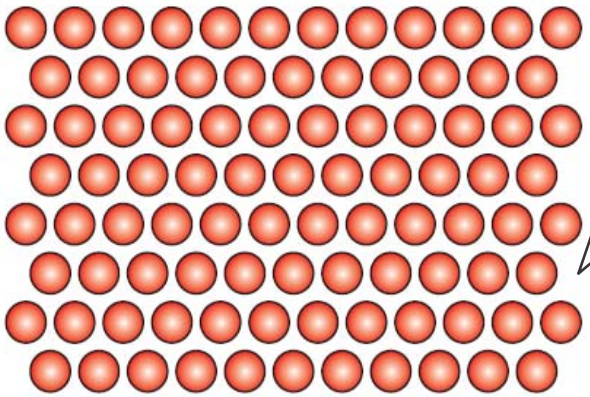


http://w3.rz-berlin.mpg.de/~rammer/surfexp_prod/

Surface specific structures

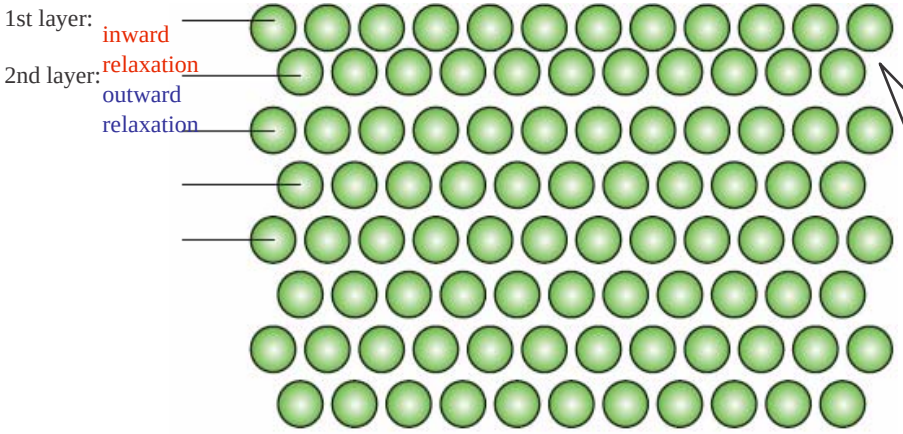
Surface relaxations and reconstructions

Bulk-truncated surface



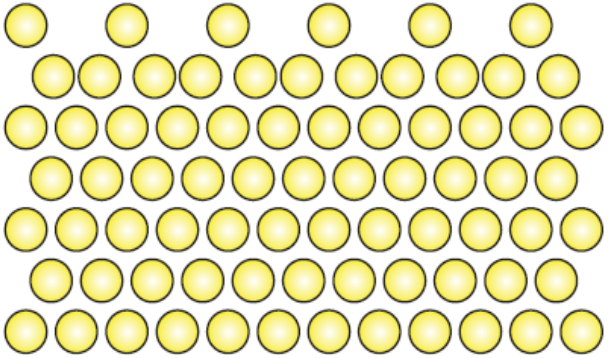
Examples:
in reality, none.
Alkali halides come close
(e.g., KF)

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



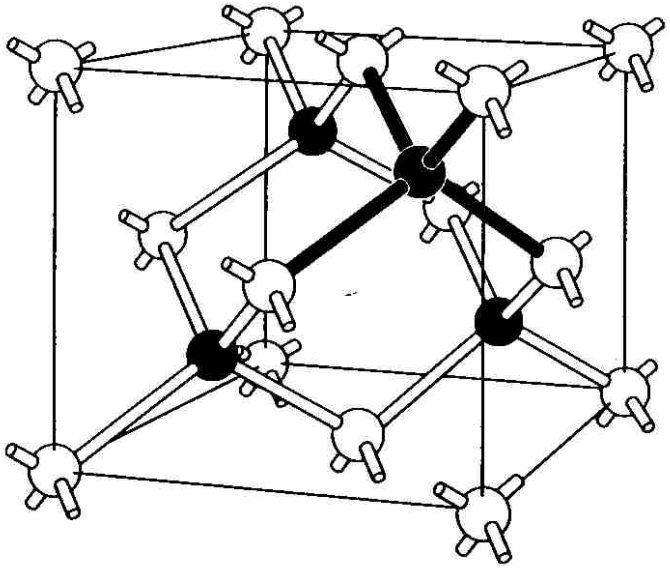
Examples:
Ag(111)
Ag(110)
Cu(111)

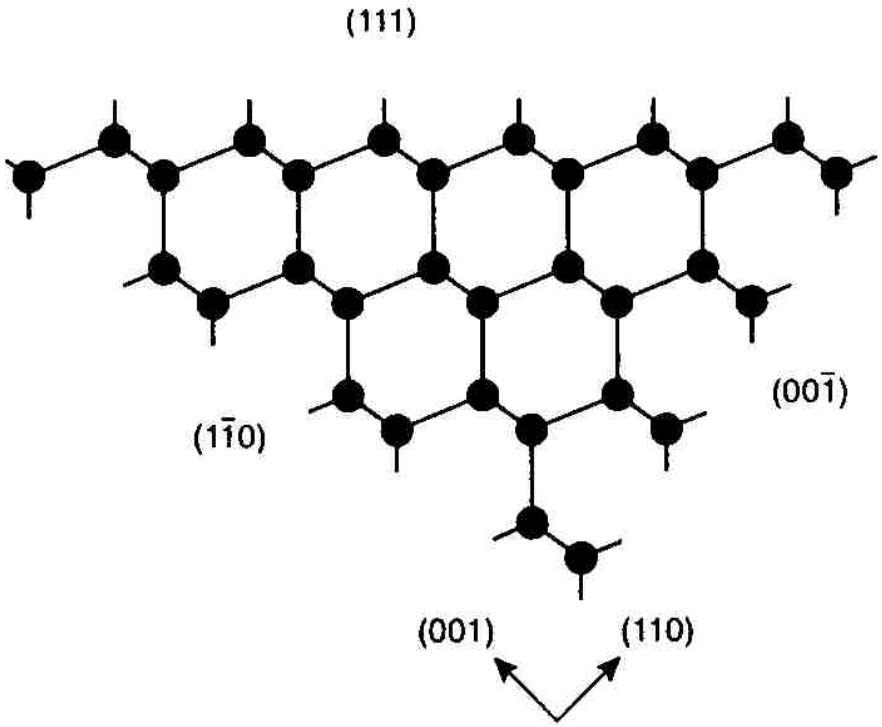
Reconstructed surface



Examples:
Au(111)
Rh(110)
Si(111)

Dangling Bonds in Si, Ge, C, GaAs (sp^3 Hybrid)

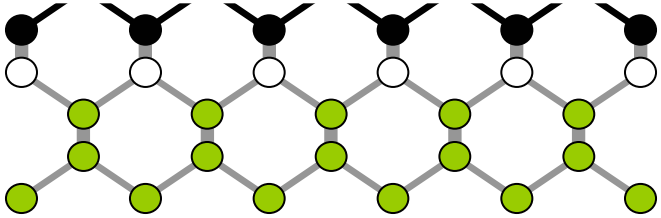


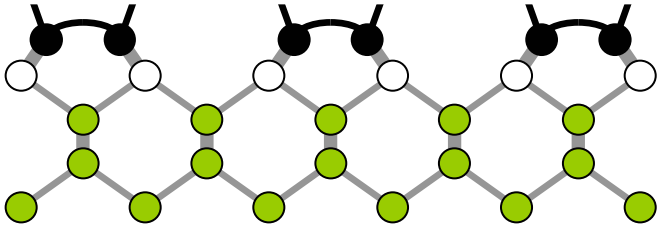


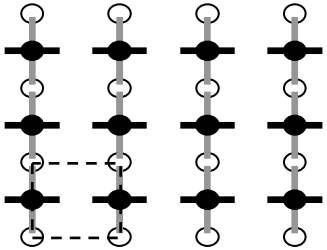
Silicon (001) Reconstruction

Two neighboring surface atoms move closer to form a "dimer bond"

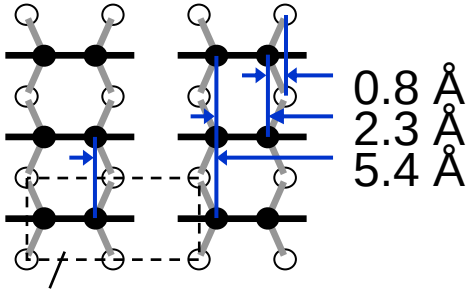
→Each surface atom now has one dangling bond instead of two





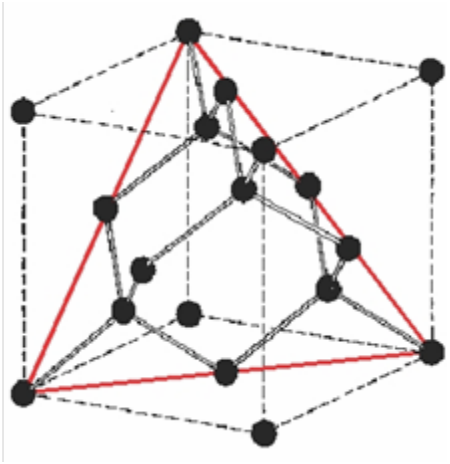


Over et al. Phys. Rev. B **55** (1997) 4731



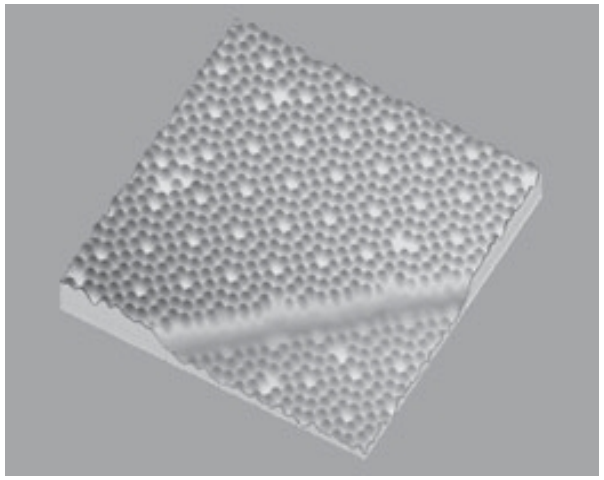
Surface unit cell

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

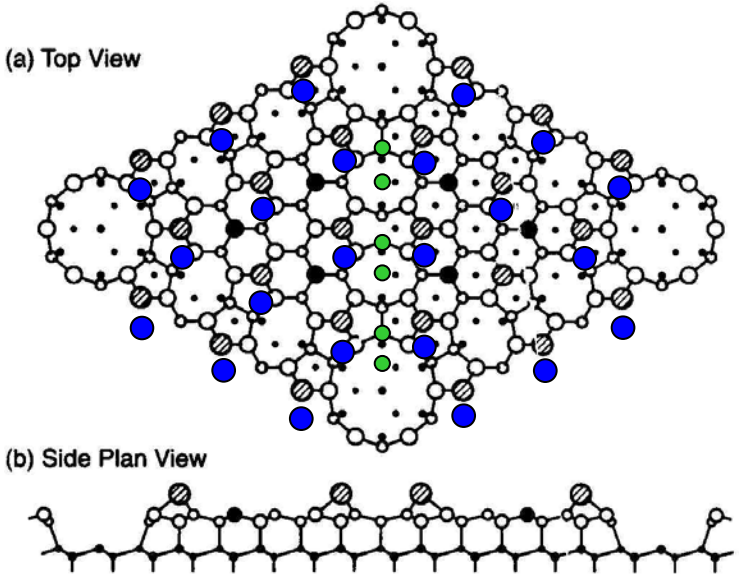


Bulk Si: diamond structure
Cut in the (111) plane

STM image

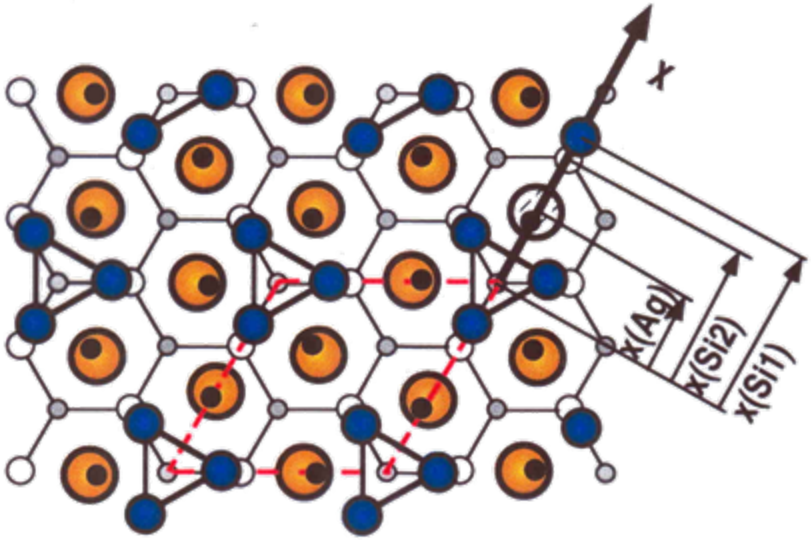


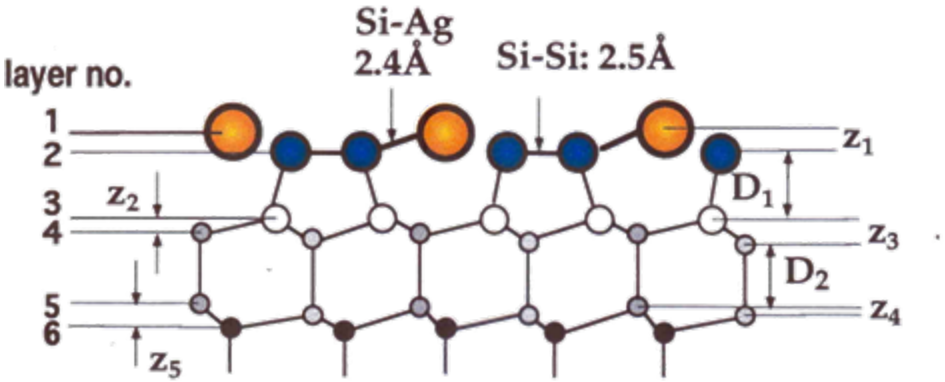
DAS (Dimer-Adatom-Stacking-fault) model



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

Si(111)-(√3x√3)R30°-Ag





Si-trimer

Ag-atoms

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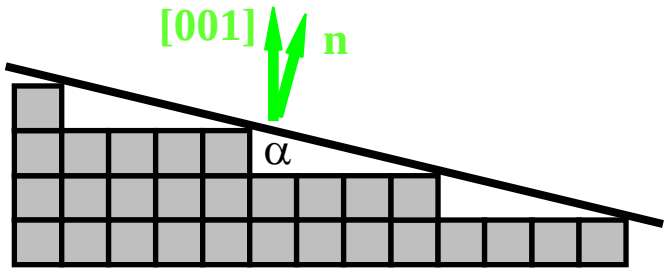
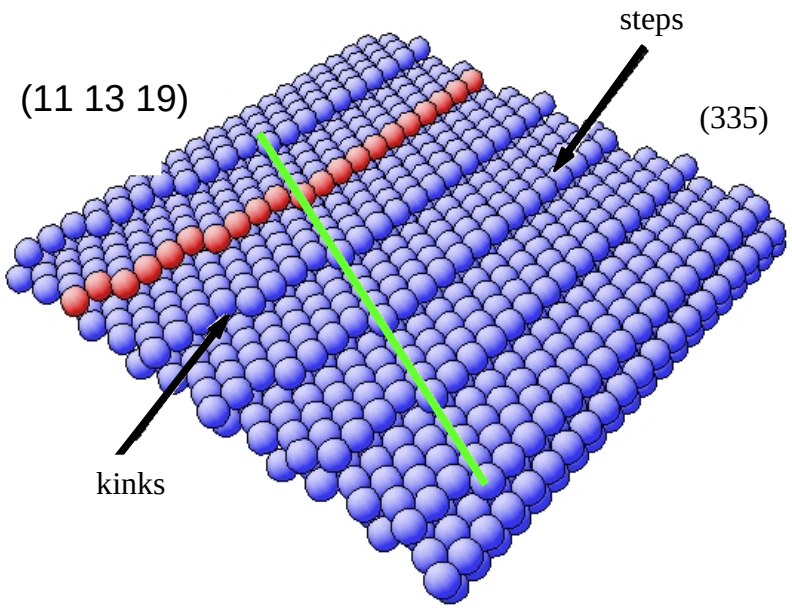
Stepped surfaces



Terraces, steps and kinks resemble low-index planes



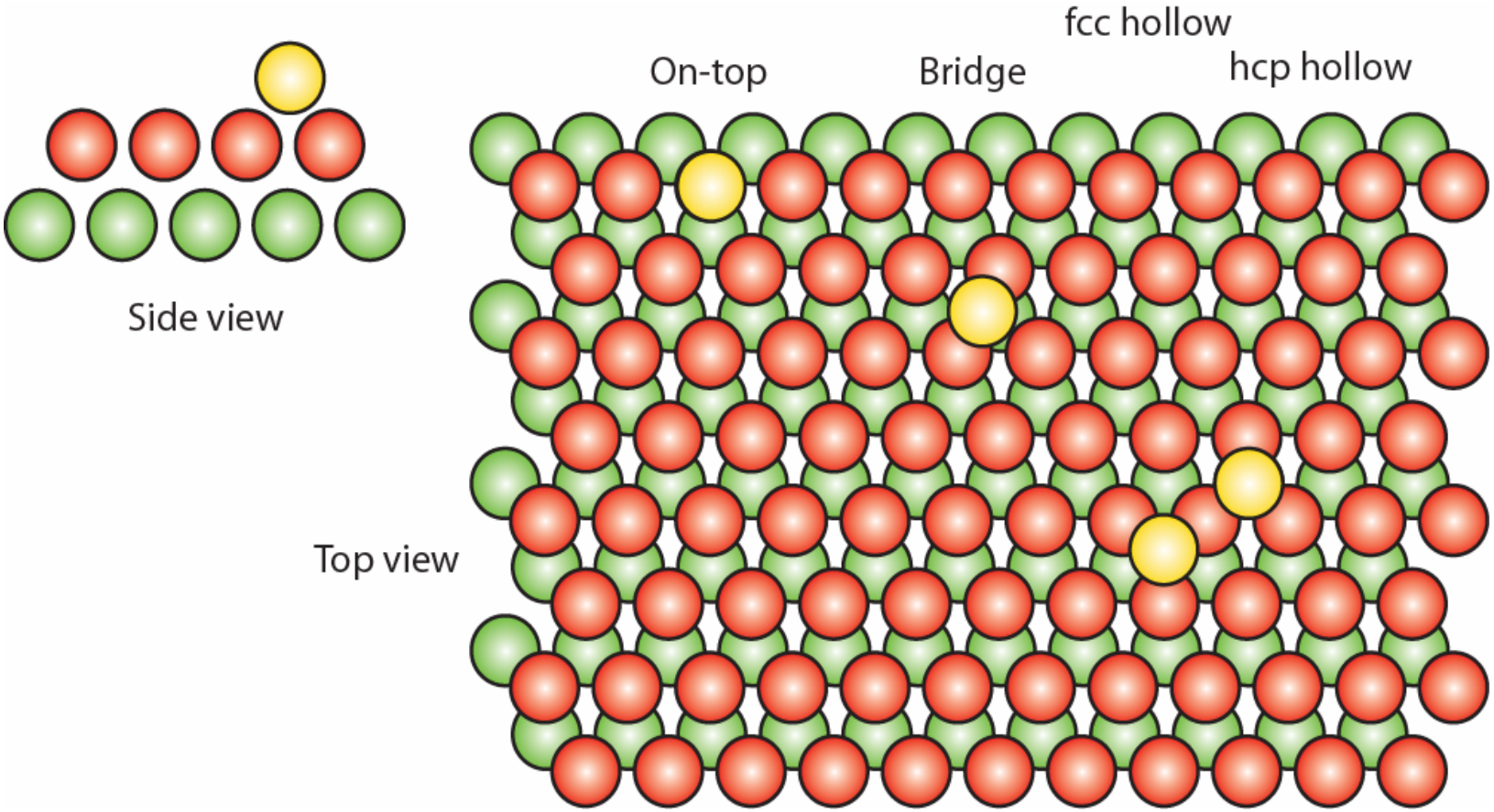
Alternative description:

n atoms wide (hkl) terrace & (hkl) step

Correspondence between Miller indices and step notation not trivial!

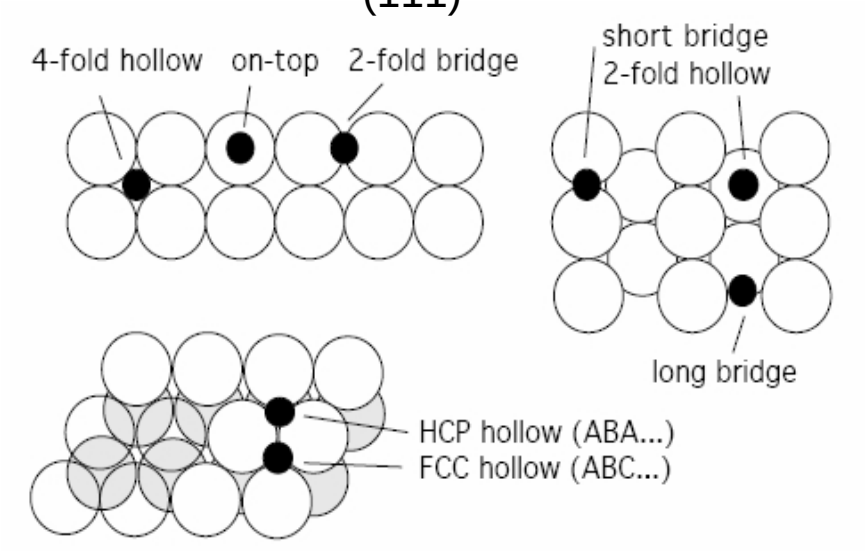
Low miscut surfaces often called vicinal surfaces

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

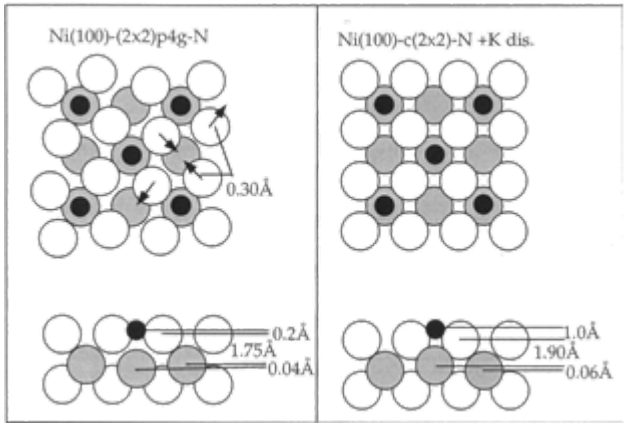


Adsorbate overlayers and induced reconstructions

Simple adsorption sites on (100), (110) and (111)



N-induced clock/anticlock reconstruction



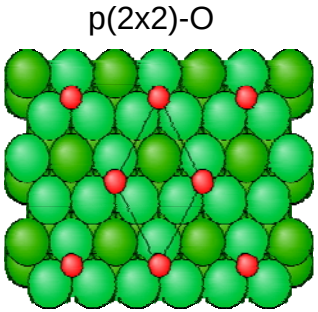
- Adsorbates can form ordered overlayers, islands, domains

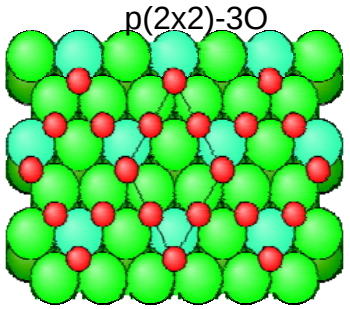
-Coverage is often measured in monolayers

1ML = (#adsorbates/primitive unit cell)

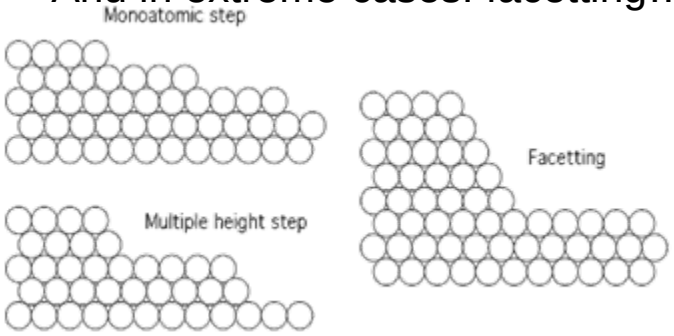
= (#adsorbates/surface atom)

- Different reconstructions/overlayers can lead to the same periodicity!

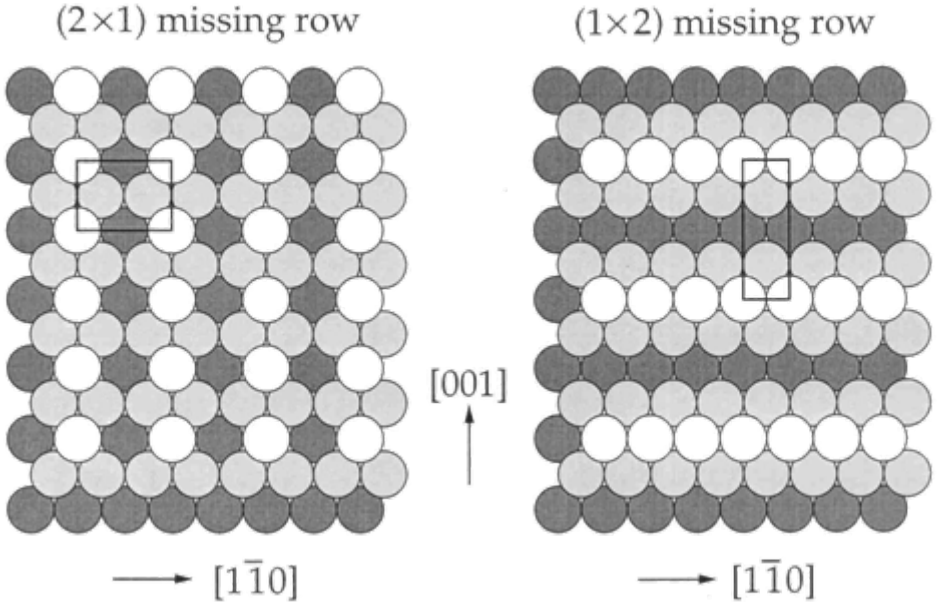


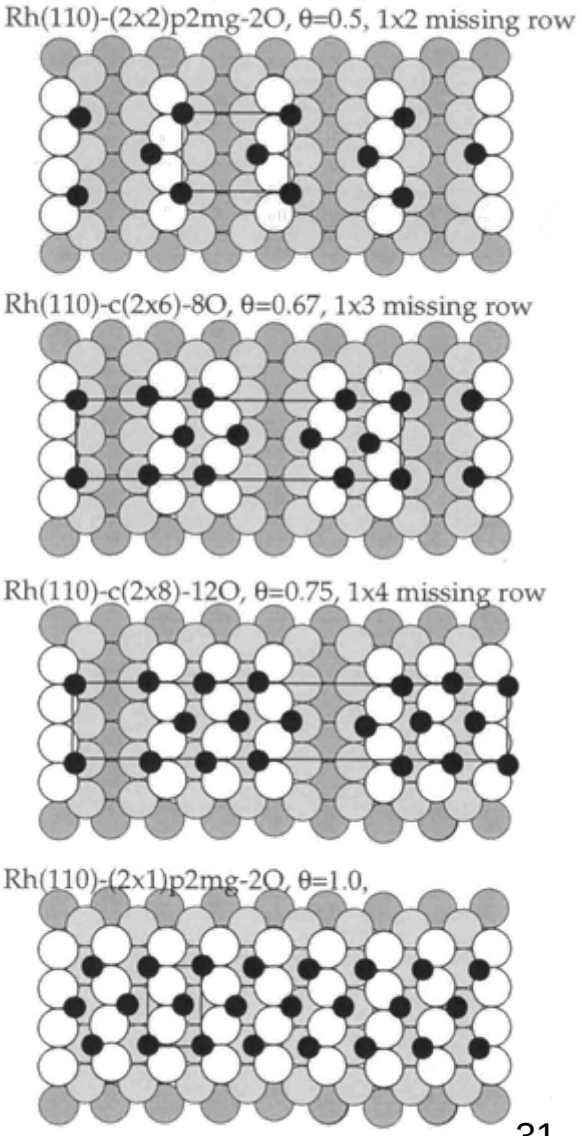


And in extreme cases: facetting…



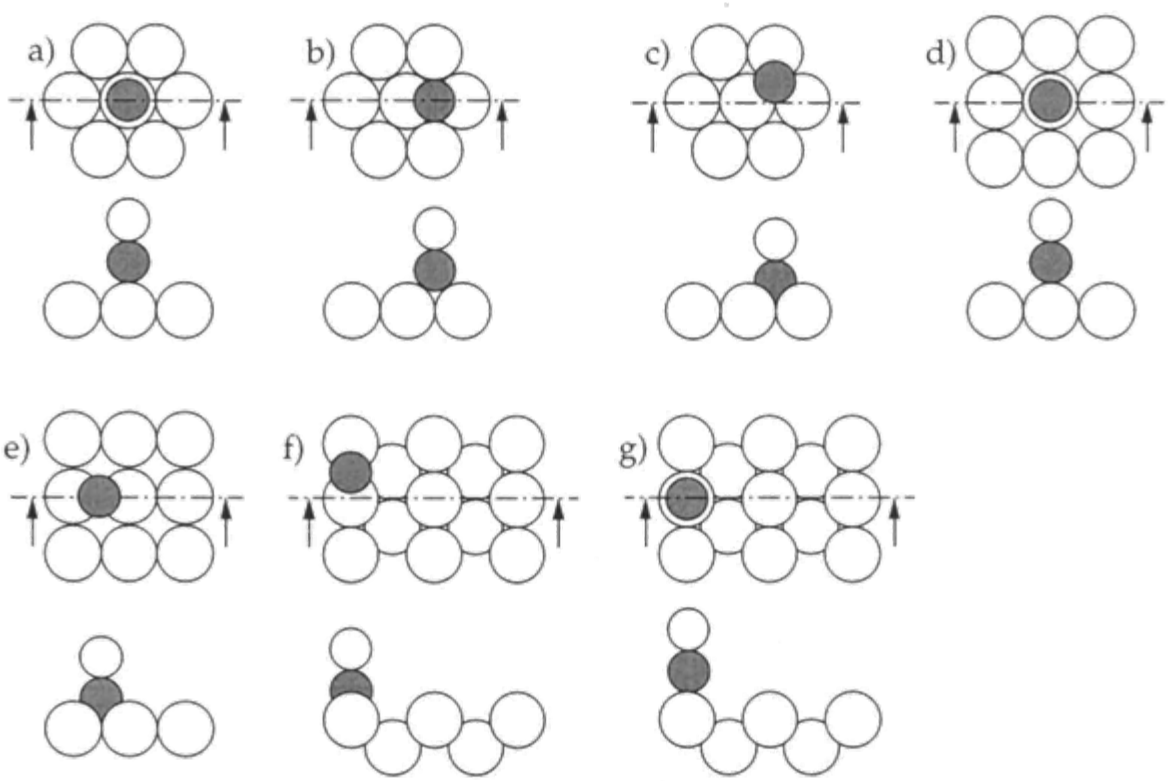
Missing Row Reconstructions on fcc(110): O-induced reconstruction on Rh(110)





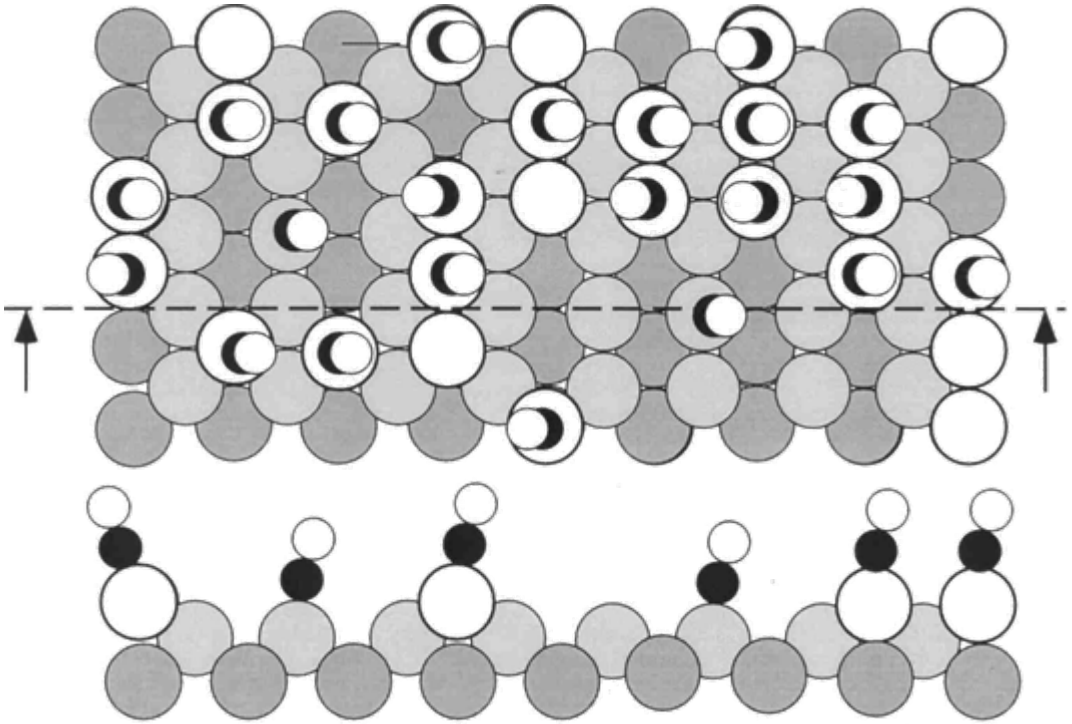
H. Over, Prog. Surf. Sci. **58** (1998) 249

CO Adsorption on various surfaces



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

CO Adsorption on Pt(110)



Schwegmann, Tappe, Korte, Surf. Sci. **334** (1995) 55