

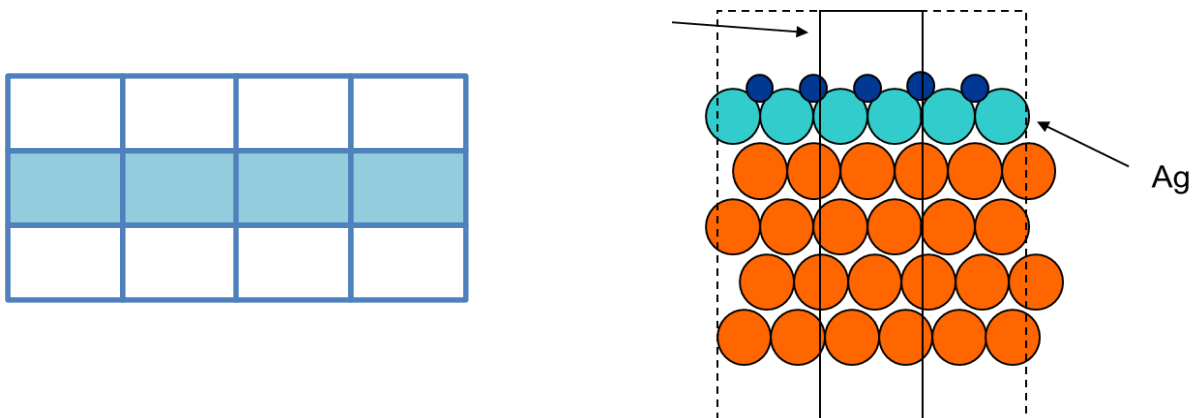
Computational Chemistry 2 – Chapter 4

Surfaces

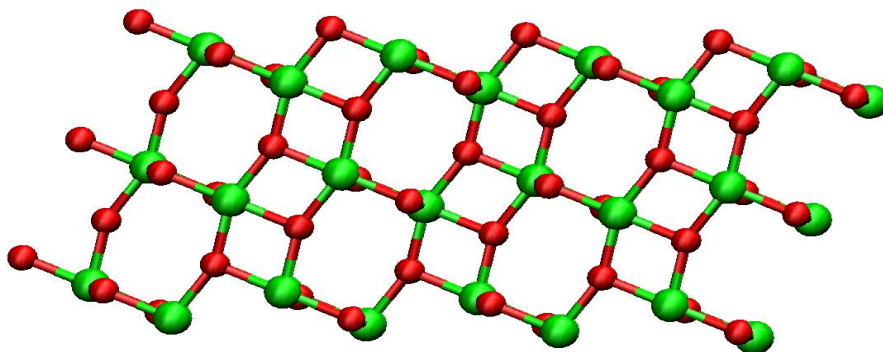
The next application is surfaces. The real surfaces will be modelled as thin periodic foils. In such system there is periodic boundary conditions in x- and y-directions. In the z-direction the periodic boundaries are not needed but in some codes, like VASP, they are used. GPAW can handle 2-D periodic systems.

The construction of the surfaces is usually easy. One needs to repeat the unit cell in every direction and then cut the "material" in certain direction. The cutting is done for the upper and lower surface. With this principle any surface of any material can be done.

The simple metal surfaces are easy. Try the ag tool in Wihuri.

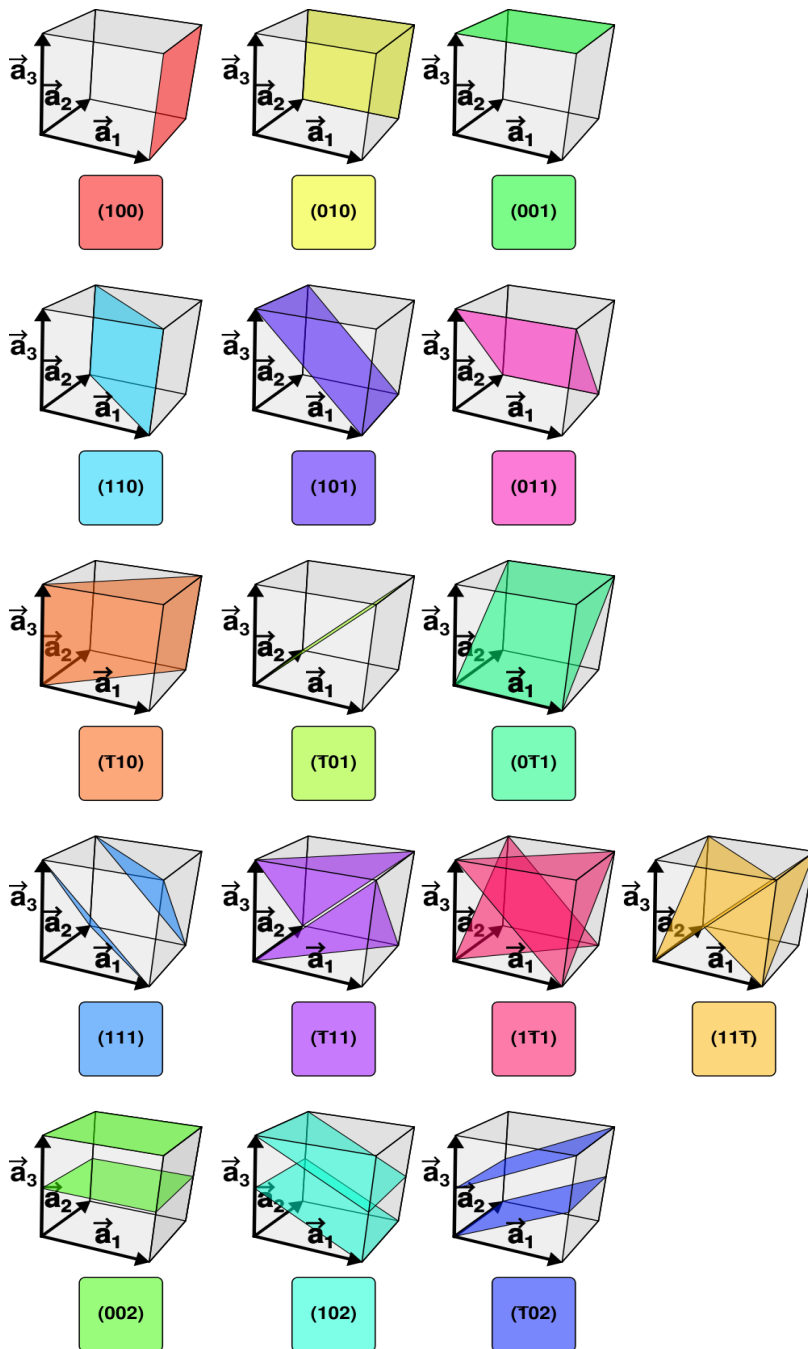


The oxide materials are less easy. Below is the TiO₂ Anatase (110) surface



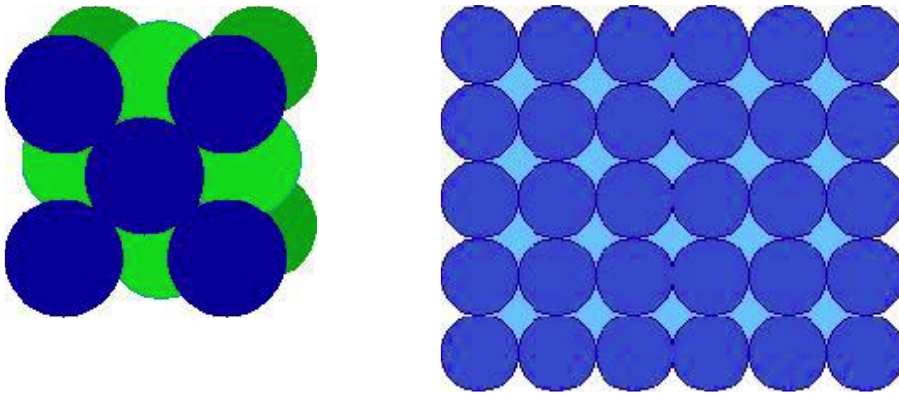
Classification of surfaces

We need to go a bit deeper to surface classification. All surfaces can be classified with Miller Indexes. The basic idea is that from a certain crystalline material one can make an infinite amount of materials by cutting the crystal in different ways. The cutting plane will be classified with the normal vector of the surface. The normal vector is given in units of the lattice vectors.

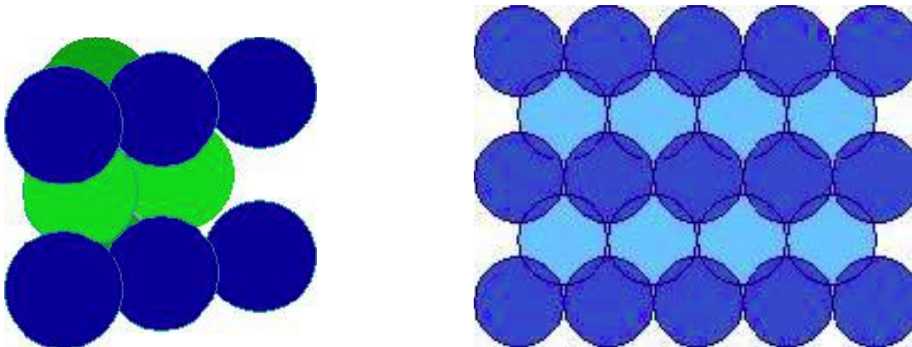


Lähde: Wikipedia, Miller_index

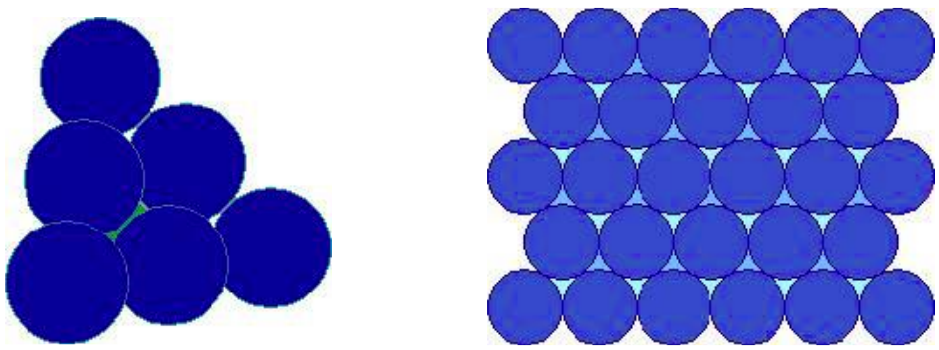
The Miller index is very simple. The (100) surface means that surface is in the (a_2, a_3) plane. Next we need to define the crystal symmetry. The FCC symmetry is very common for pure metals. We can look how the low Miller index surface will look for FCC material. (The FCC is the face centered cube structure. In it the atoms are in the corners of the cube and in the middle of the faces). The fcc(100) surface is along face of the cube. Note that the picture at right is rotated by 45 deg. (it the left the dark blue is the first atomic layer and the light blue the second.)



The (110) surface will look as following. It is very open. There are atomic rows and between them the next atomic layer is clearly visible.



The (111) surface is the most compact. In the picture very little light blue is seen.



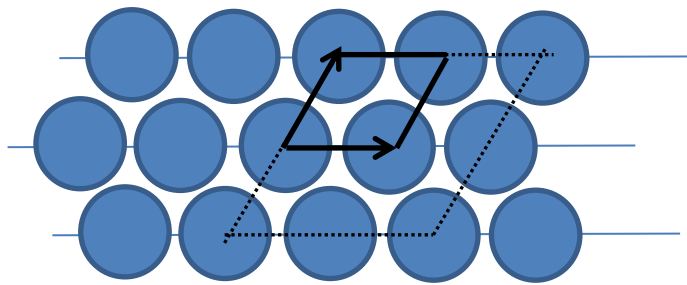
The Miller index is very useful way to characterize the surfaces but one has to remember that the picture of the surface depends also on the lattice.

Surface unit cell

As in the bulk there is also a unit cell on the surface. The unit cell is the symmetric unit that repeats over the surface.

Example: the ideal FCC(111) surface unit cell

What kind of unit cells do the other FCC surfaces have?



Very often the surface unit cell is larger than the ideal unit cell. The larger cells are marked with the multiplicity of the unit cell. (2x2) means that the surface unit cell is twice of the ideal cell in x and y direction. See below. The surface unit cell can be rotated

with respect to the ideal one. Then the notation is $(axa)R\theta$. The θ is the rotation angle of the cell.

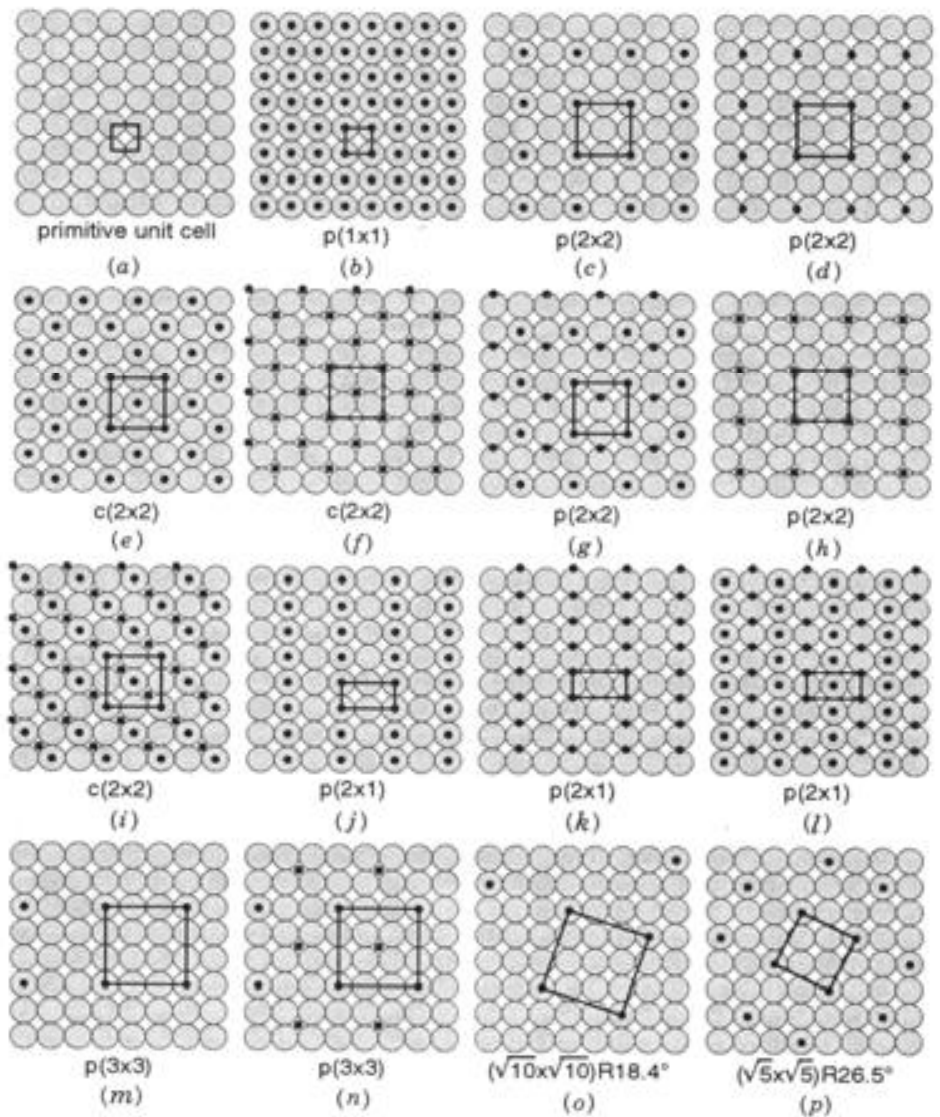
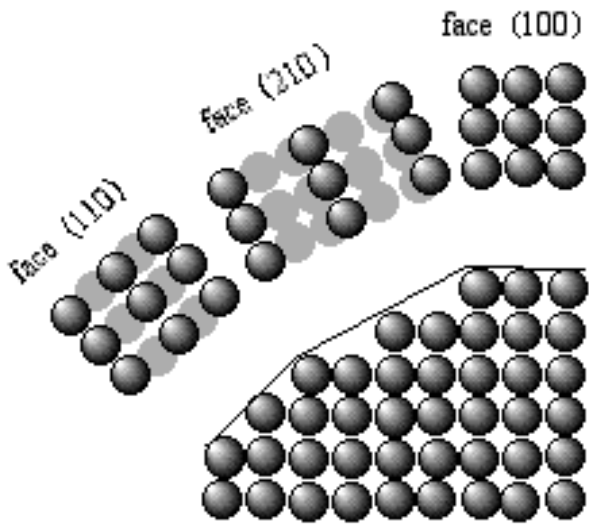


Figure 2.71 Wood's notation for a number of overlayers on the (100) face of an FCC metal.

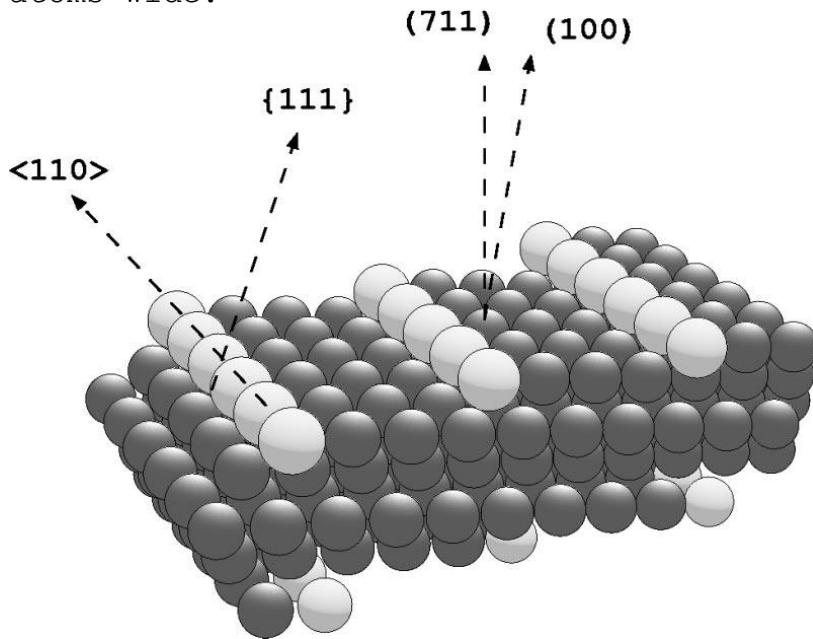
Some times a letter c or p is put in front of the cell. P means that there is not extra symmetry (the p is often omitted). The c means that there is an atom in the centre of the cell.

Stepped surface

The surfaces above are the simple ones but more complicated ones can also be constructed using the Miller index. The most interesting are the stepped surfaces.

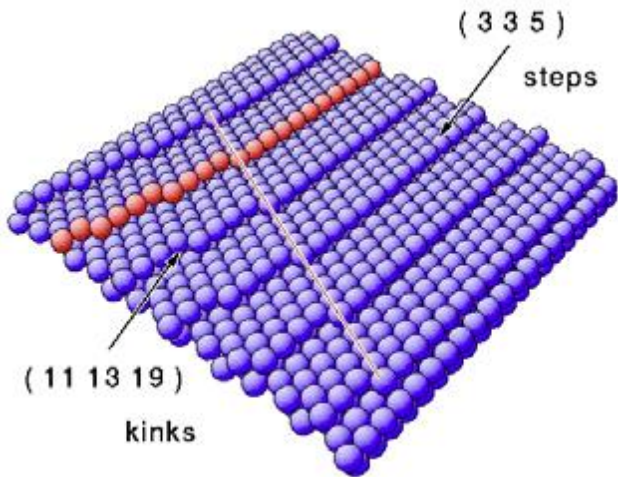


Below is a picture of the FCC(711) surface. (711) surface consist of atom height steps which have (100) structure. The steps are ca. 4 atoms wide.



Picture: FCC:n (711) surface. Source: PHYSICAL REVIEW B 64 094403 (2001)

Also tilted steps can be constructed using high Miller indexes. Below is the (11 13 19) surface and comparison to (335) surface.



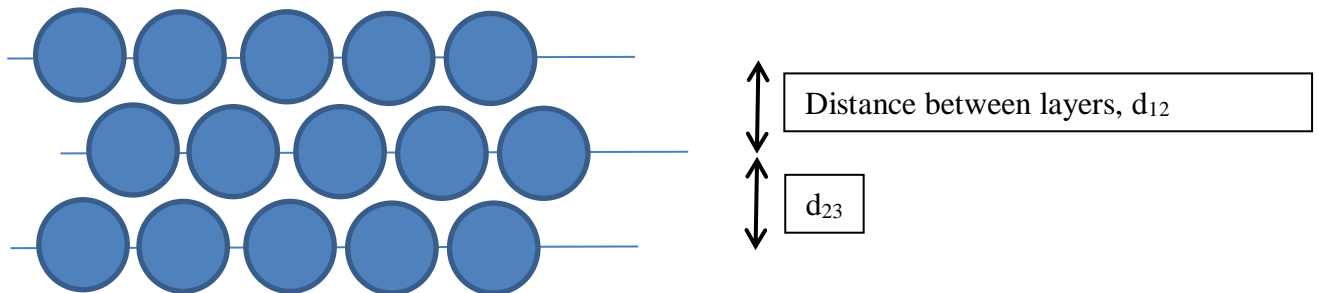
Surface energy

The surface energy is easy to compute. If we have (nmk) surface and the systems have N atoms its energy:

$$E_{\text{surf}} = E_{\text{nmk}} - N E_{\text{atom,bulk}}$$

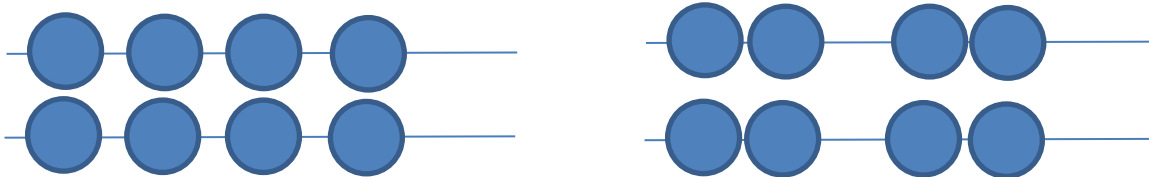
Relaxation and reconstruction

When the surface is made the coordination numbers of the atoms change. This will cause the atoms to move. On surface the atoms are never in their crystalline positions. The simplest movement is the relaxation where only the atom layers will move. There might be small variations in the height but the (x,y) positions will not move and thus the surface symmetry do not change. The relaxation is typical for close-packed surfaces, like FCC(111).

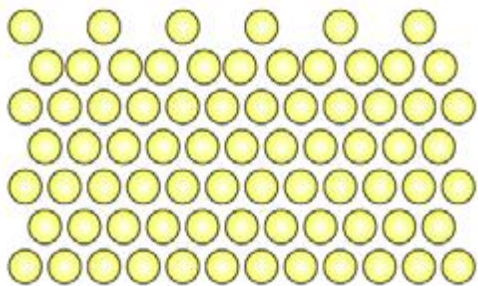


Of course the atoms can move in the (x,y) plane. This is called reconstruction. (Naturally the reconstruction always cause some relaxation.) The reconstruction can be simple, when two atoms move closer to each other. The reconstruction will always change the surface unit cell.

Exercise: What the symmetry of the pairing reconstruction.

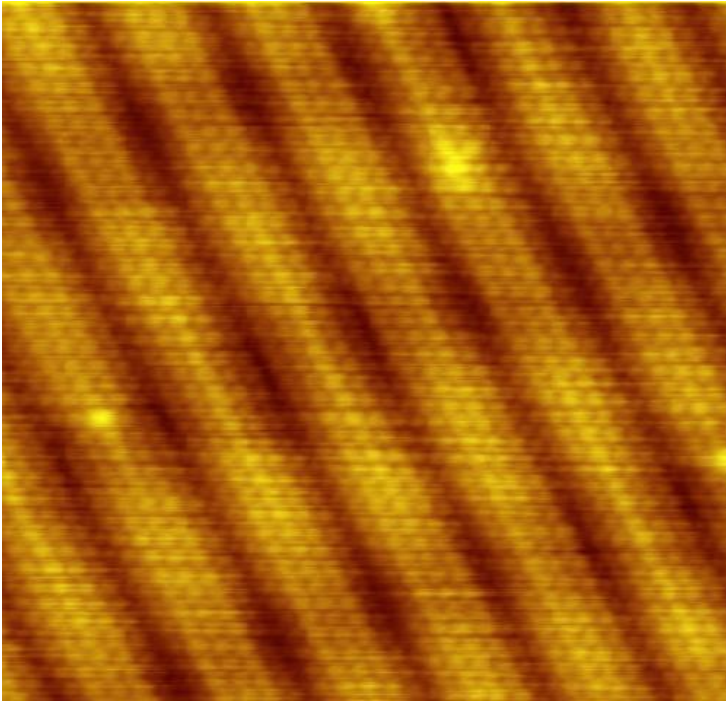


One rather common reconstruction type is missing row reconstruction. In this case every n'th atomic row are missing from the surface. In common missing row reconstruction every second row is missing. This known in Au(111) surface.

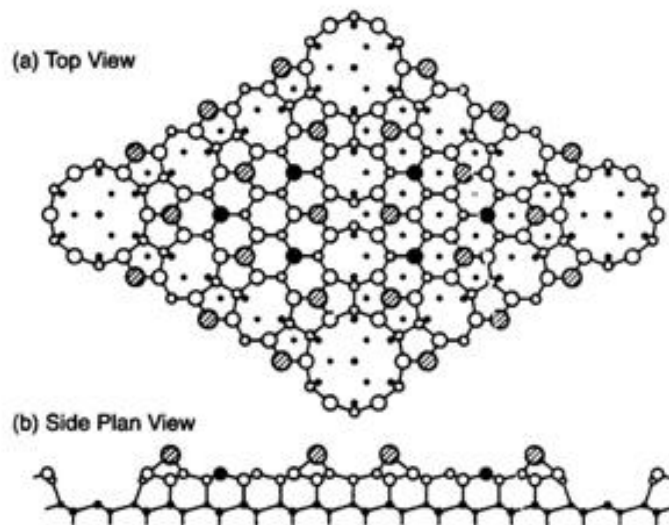


Au(111)

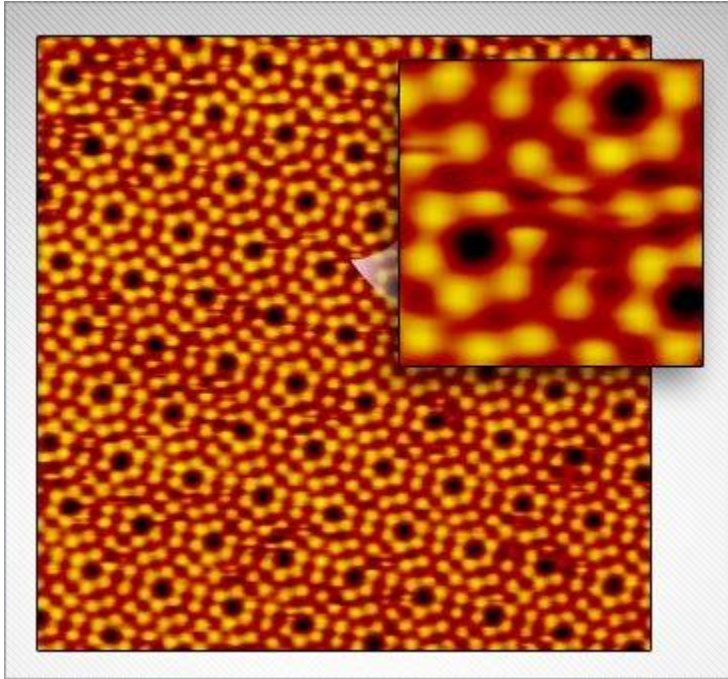
In Au(100) the reconstruction is rather complex, it reconstruct into a distorted hexagonal structure. The surface symmetry is (28×5) and it is rotated by about 0.81° relative to [011] crystal direction.



Another very complex reconstruction: Si(111) (7x7) reconstruction



Note that all reconstructions considered here happen on clean surfaces when an adsorbent (molecules or atoms) is added new reconstructions can happen.



A STM image of the Si(111)(7x7) reconstruction (From: <http://www.rhk-tech.com/si111-7x7-reconstruction/>)