

**SOLID SURFACES**

**&**

**INTERFACES**

## Introduction – Relevance

- It's a cross-disciplinary field of science and engineering: physics, electrical engineering, material science and chemistry;
- They play a central role in many everyday phenomena, such as:
  - charge transfer between 2 materials brought into contact – *triboelectricity*
  - oxidation of materials - *corrosion*
  - Use of protective layers – *passivation*
  - Wetting of surfaces and dispersion of particles in fluids like paints and time-release capsule medicines – *colloid chemistry*
  - Friction between sliding objects in contact and their lubrication - *tribology*
  - Removal of surface layers – *cleaning and chemical etching*
  - reduction in energetic barriers to speed up or improve the yield of chemical reactions - *catalysis*
  - Rainbow of colors reflected off thin oil layers or from layered materials – *optical interference*
  - electromagnetic interfaces between Earth's atmospheric layers responsible for the bouncing and radio wave transmission around the world.
- They play a major role in electronic technologies! Manipulation of interfaces can change charge transfer and atomic diffusion processes and change the conduction properties of such semiconductor devices.
- They have an even higher impact when such devices are dimensioned to operate in the quantum regime – quantum electronic devices: *the quantum well* is one of the basic components of optoelectronics.

## Definitions

**Solid Interface:** small number of atomic layers that separate two solids in close contact with one another, where the properties differ significantly from those of the bulk material it separates.

**Surface of a solid** is a particularly simple type of interface, at which the solid is in contact with the surrounding world, i.e., the atmosphere or, in the ideal case, the vacuum.

The development of modern interface and thin film physics is thus basically determined by the theoretical concepts and the experimental tools being developed in the field of surface physics, i.e., the physics of the simple solid–vacuum interface.

Surface physics itself has mean-while become an important branch of microscopic solid-state physics, even though its historical roots lie both in classical bulk solid state physics and physical chemistry, in particular the study of surface reactions and heterogeneous catalysis.

# Study of Surfaces & Interfaces

## Morphology

- macroscopic form or shape of a surface or interface.

Macroscopic approach



Thermodynamics

## Structure

- microscopic, atomistic picture used to denote the detailed geometrical arrangement of atoms and their relative positions in space.

Microscopic approach



Atomic structure

Macroscopic approach



Thermodynamics

Basic concepts in this context:

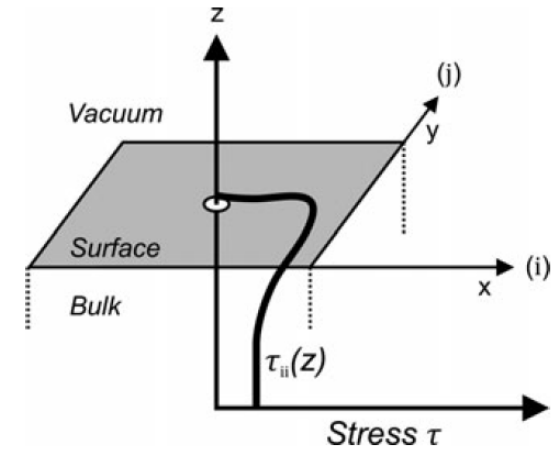
- **free specific energy** of a surface or interface and that of **surface stress** or *surface tension*.
- When a surface is created, the electrons respond to the absence of atoms above the surface so that the charge distribution near the surface (chemical bonds) becomes different from that in the bulk. On the atomic scale forces on the atoms in the topmost atomic layers are changed with respect to the bulk situation.

## Variation of the Stress tensor

The stress tensor  $\tau_{ij}$  therefore varies along an axis  $z$  perpendicular to the surface within several atomic distances:

- $\tau_{ij} > 0$  – positive if the surface contracts under its own stress, i.e., work is required to stretch the surface elastically (tensile stress).
- $(\tau_{ij} \leq 0)$  : Negative surface stress is called compressive.

Typical surface stresses of solids are of the order of **1 N/m** and are confined to typical distances of **1 nm** from the surface.



## Variation of the Surface Free energy

The surface free energy  $F^{(s)}$  may change by two different contributions:

$$\delta F^{(s)} = \delta(\gamma A) = \gamma \delta A + A \delta \gamma$$

- When  $\gamma$  stays constant but the surface area changes by  $\delta A$  (first term), the number of surface atoms is changed with a fixed average area per surface atom.
- The second contribution  $A \delta \gamma$  describes the effect that the number of surface atoms remains constant but their energy, i.e., the interatomic distances in a reconstruction change, varies.

## Bringing the 2 to together

$$\tau_{ij}^{(s)} = \gamma \delta_{ij} + \frac{\partial \gamma}{\partial \varepsilon_{ij}} \quad \longleftarrow \quad \text{Shuttleworth equation}$$

By re-arranging the terms:  $\partial \gamma / \partial \varepsilon = \tau^{(s)} - \gamma$ , we may consider as the thermodynamic driving force to move atoms from the bulk into the surface layer.

- $\tau^{(s)} - \gamma > 0$  the surface wants to accumulate more atoms than are found in the bulk in a comparable volume;
- $\tau^{(s)} - \gamma < 0$  the surface prefers less atoms in the surface layer.



## NOTES about the Surface Energy

- the surface energy  $\gamma$  may be regarded as an excess free energy per unit area;
- It is the reversible work of formation of a unit area of surface or interface at constant system volume, temperature, chemical potential, and number of components, which implies that the composition and atomic configuration in the interface region are those of thermodynamic equilibrium.
- Considering a crystalline structure with its surface next to air/vacuum, it costs energy to generate an additional piece of surface while keeping the crystal volume and the number of constituent atoms constant.
- Bonds between neighboring atoms must be broken in order to expose new atoms to the air/ vacuum. The formation of surface defects including steps might also be involved in forming the new surface area. All these effects contribute to the excess surface free energy  $\gamma$ .

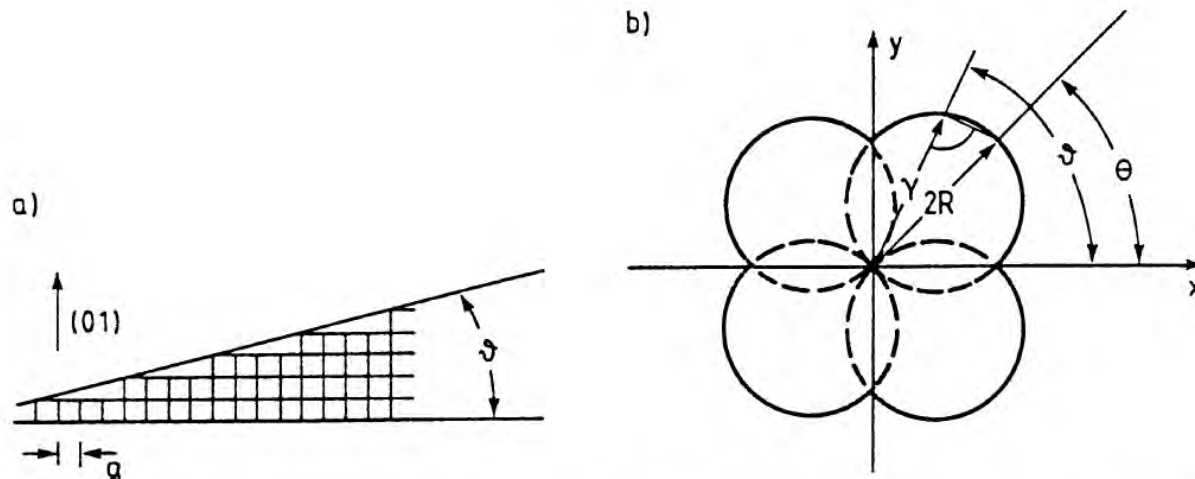
## Free Energy & Surface orientation

- For crystalline materials, most surface properties depend on the orientation. In particular, depending on the surface orientation ( $hkl$ ) more or less bonds have to be broken to create a piece of surface....
- The surface free energy of crystals  $\gamma$  ( $\mathbf{n}$ ) is therefore strongly dependent on the orientation of the particular surface,  $\mathbf{n}$ .
- The equilibrium shape of a crystal is not necessarily that of minimum surface area, it may be a complex polyhedron.
- If there are certain lattice planes with particularly low surface energy, a surface can lower its total free energy by exposing areas of this orientation. Even though facetting produces an increase in total surface area, it may decrease the total free energy and is sometimes thermodynamically favored.

In the theory for the crystal equilibrium shape and morphological stability can be determined by a rough model called the,

**Wulff plot** of  $\gamma(\mathbf{n}) = \gamma(hkl)$

$$\gamma = 2R \cos(\theta - \Theta) = 2R[\cos \Theta \cos \theta + \sin \Theta \sin \theta]$$



**Fig. 3.3** Schematic drawing of surface and simple Wulff plot (surface energy  $\gamma$  in polar coordinates) for a vicinal surface plane with inclination angle  $\theta$  against [01] consisting of areas with [01] orientation (a). The Wulff plot (b) consists of circles passing through the origin

➤ The length of the vector from the origin to a point on the plot represents the magnitude of  $\gamma(hkl)$ , and the direction is that of the normal to the  $(hkl)$  plane.



- Thus a surface is not merely a truncation of the bulk of a crystal.
- The distortion of the ideal bulklike atom configuration due to the existence of a surface will be different for metals and for semiconductors.
- In metals we have a strongly delocalized electron gas and a chemical bond which is essentially not directed, whereas in tetrahedrally bonded semiconductors (Si, Ge, GaAs, InP, etc.) significant directional bonding is present.
- Bond breaking on one side due to the surface is expected to have a more dramatic effect on the atomic configuration at the surface of a semiconductor.

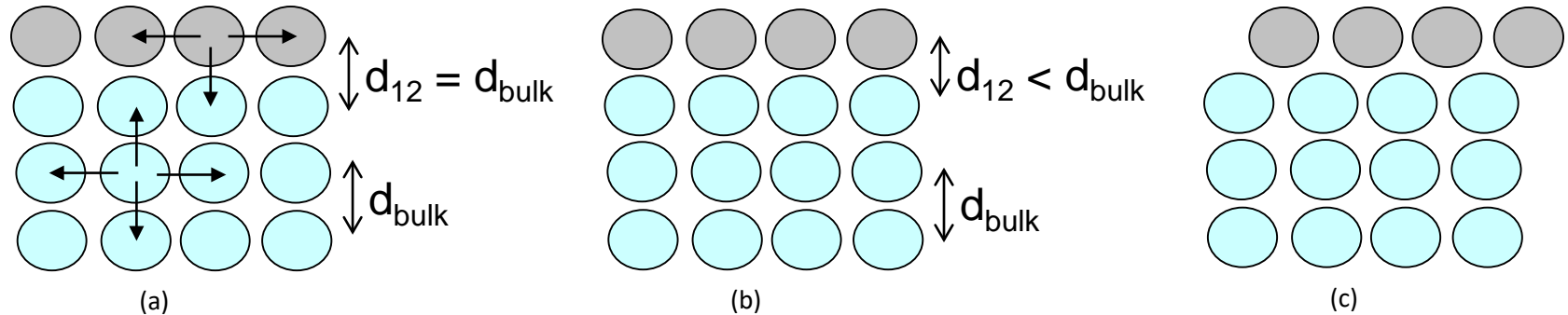
## Surfaces Reconstruction

- The presence of the surface destroys the translational invariance of the crystal, near the surface.
- Atoms near the surface can change their bonding because of the lattice termination.
- Semiconductors with diamond (Si, Ge) and zincblend structures (GaAs) show reconstructions of the outer atomic layers due to :

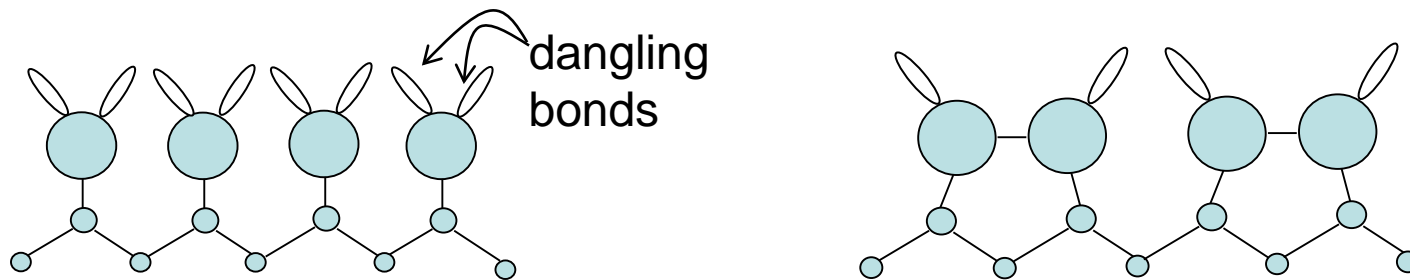
lattice termination and redistribution of bond charge.

- Surface reconstruction simulations and measurements showed that bond length changes are small at the surface; reconstruction is due primarily to bond rotation. Bond rotation is characteristic of III-V and II-VI compounds.
- The driving force for such reconstructions is the minimization of surface energy.
- Surface bond energy minimization depends primarily on geometric structure rather than the detailed electronic structure.

# Surface Relaxation and Reconstruction



In surface relaxation, atoms in the surface layer may shift inwardly or laterally



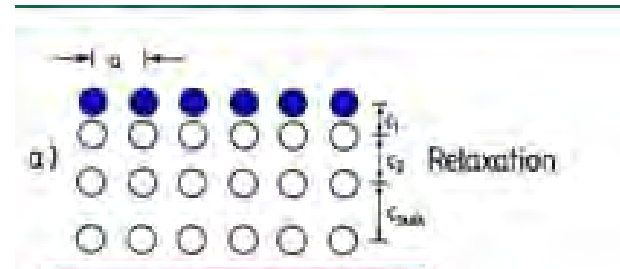
Dangling bonds may combine to form strained bonds between themselves, the surface layer is *reconstructed* with different bond lengths and/or angles.

Surface atomic layers can have different point group symmetries, Bravais lattices and periodicities from those of the bulk crystal! The following figure shows side views of the characteristic examples of atomic re-arrangements for a simple cubic lattice of lattice constant  $a$ .

Surface atom (blue) undergo relaxation prior to reconstruction;

(a) Relaxation

The top row of atoms relax back towards the bulk so that  $c_1 < c_2$ ;



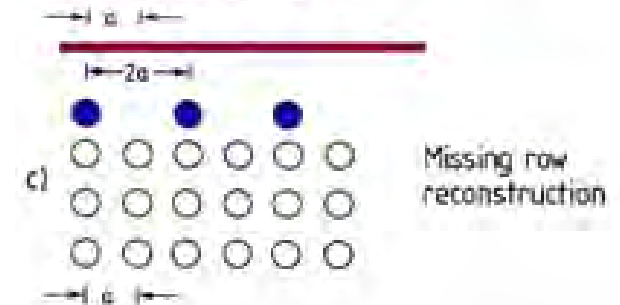
(b) (Dimer) Reconstruction

Dimerization of the top row atoms such that surface periodicity is now twice as large.



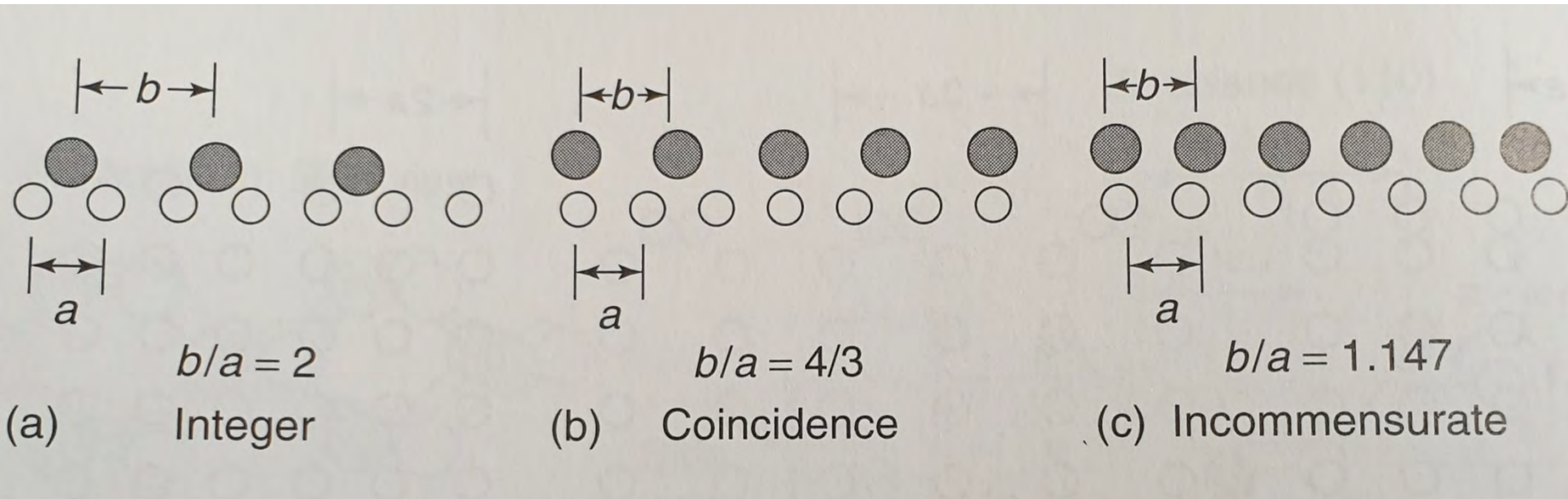
(c) (Missing row) Reconstruction

Every other atom in the top row is missing giving rise to a surface periodicity that is also now twice as large.



Surface adsorbates add another level of complexity! to the reconstruction process.

The following picture shows side views of adsorbates on a crystal lattice with different ratios of adsorbates vs. crystal lattice constants.



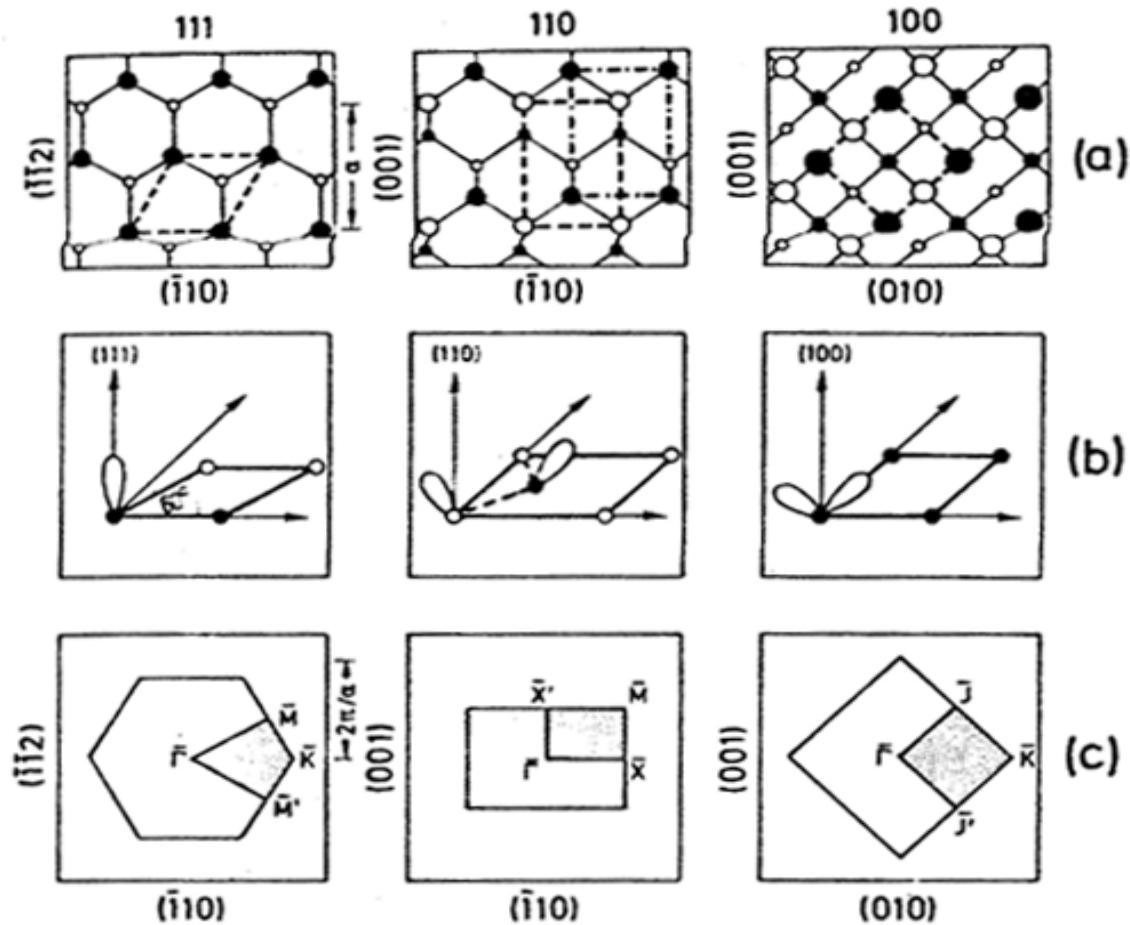
Surface lattices with a different periodicity than that of the substrate are termed:

**Superlattices**

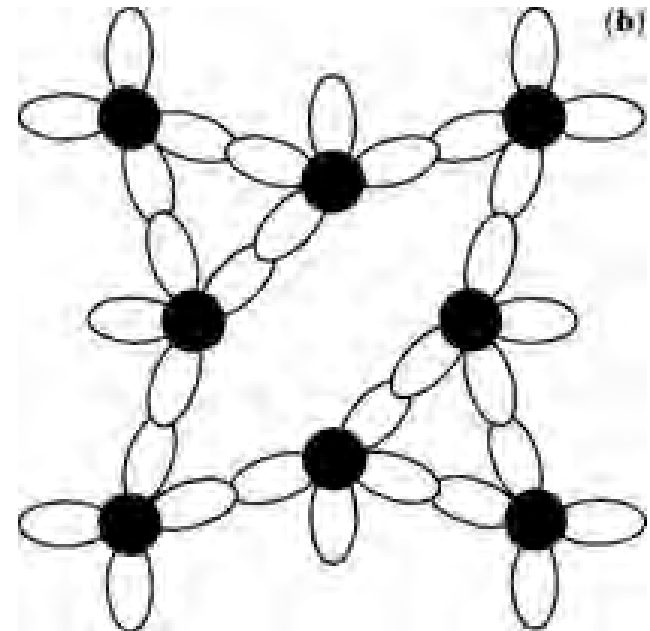
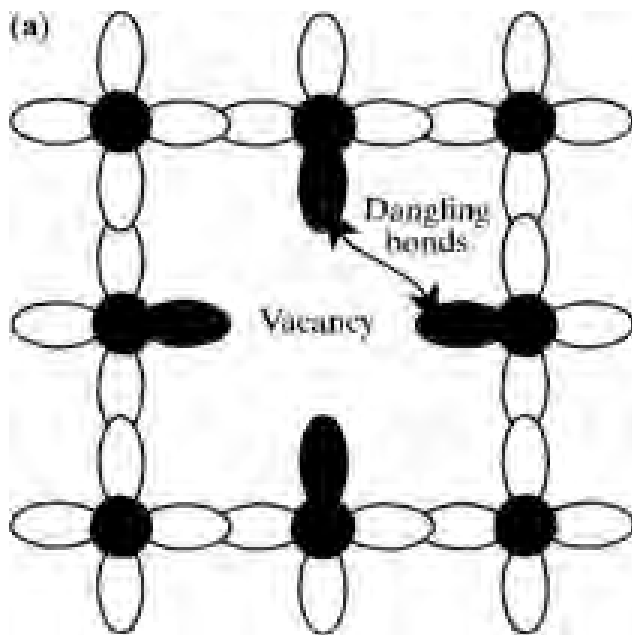
Note: the adsorbate layer can also be amorphous, interdiffused or react to form an interface compound. This is will not be covered here.



## Surface states on semiconductors after reconstruction



Each dangling bond orbital will result in a surface state for non-reconstructed surface, reconstruction complicates the situation... We can have reconstruction with or without dangling bonds remaining!



Schematic diagram of a covalent semiconductor with

- (a) an unrelaxed vacancy involving four dangling bonds and,
- (b) a relaxed vacancy with no dangling bonds

# Electronic surface states

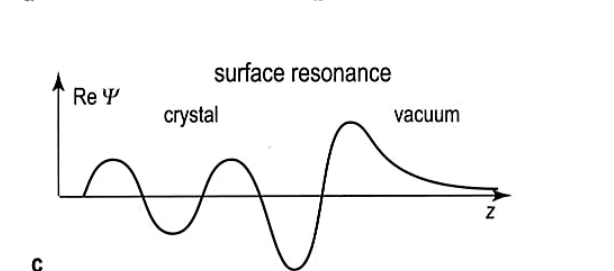
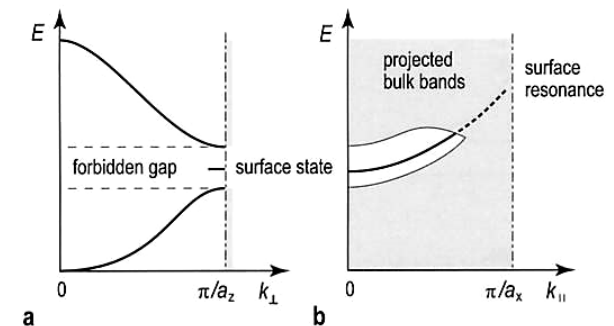
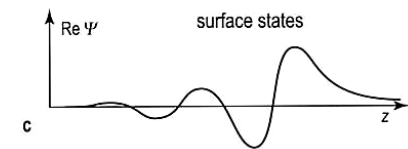
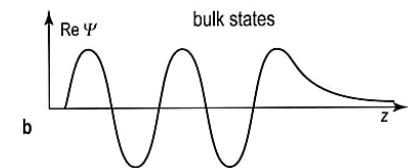
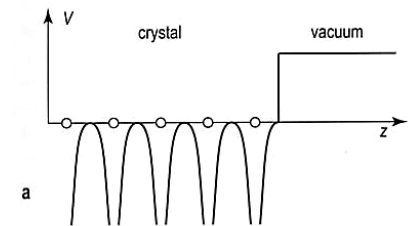
(a) The solution of the Schrödinger equation for a 1-dim. problem near a surface leads to:

(b) bulk states, which are periodical in the bulk and decay exponentially to the vacuum, and

(c) surface states, decaying exponentially both in to the bulk and the vacuum.

(a,b) The bulk states show a dispersion, whereas the surface state have a distinct value (normal to surface). But, surface states show a periodicity parallel to the surface and have therefore also a dispersion in this direction.

(c) All bulk states can be projected onto the surface, with their  $k$  vector components parallel to the surface (surface projected bulk bands).



# Si(111) – one of the most important semiconductor reconstructions!

DAS model of the Si(111)7x7 reconstruction is shown schematically in the figure.

The non-reconstructed (111) cell corresponding to the 7x7 unit cell contains 49 atoms which are all in the surface plane.

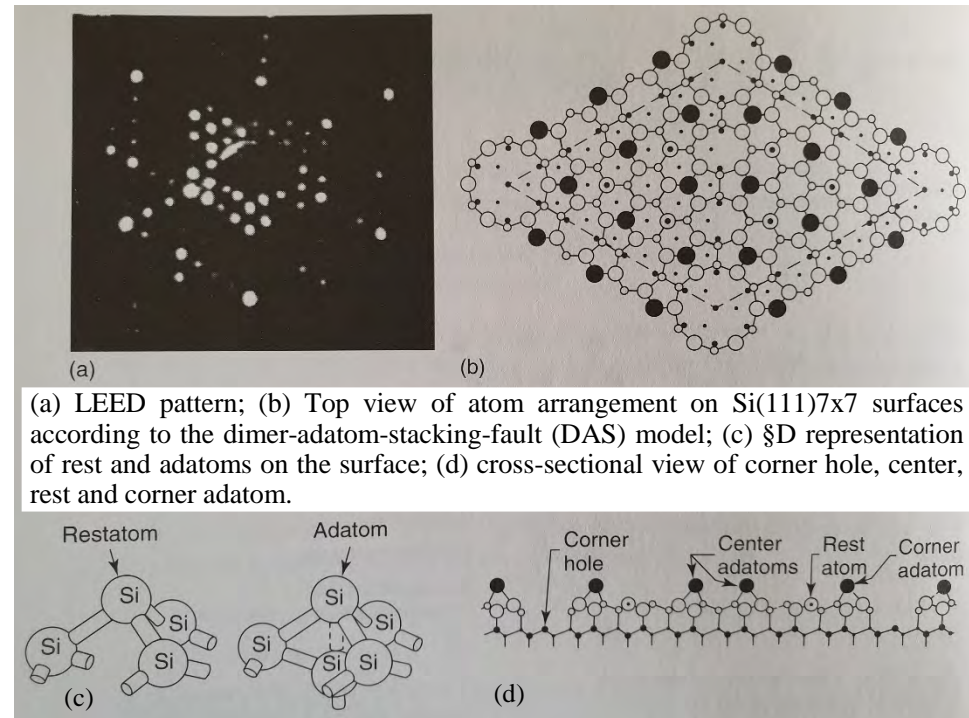
In the DAS model the energy associated with the dangling bonds is decreased by reducing their number from 49 to 19.

The top layer contains 12 atoms (the so called adatoms) while the layer below consists of 42 atoms. Due to their position, all adatoms are not electronically equivalent.

Because of a stacking fault in the unit cell, the two triangular halves are not equivalent and are referred to as faulted and unfaulted halves.

Furthermore, the reconstruction is accompanied by very large angular distortions. The dangling bonds are saturated by the adatoms, and the dimer bonds are such examples.

These distortions extend in depth to the third layer below the surface.



This complex surface reconstruction involves 3 double layers of atoms. The circles in (b) indicate atoms whose decreasing diameter correspond to positions lower down away from the surface. (c) and (d) illustrate the configuration of the various surface atoms. Extended, coherent features of the surface topology can help to minimize strain and overall energy for structural stability.

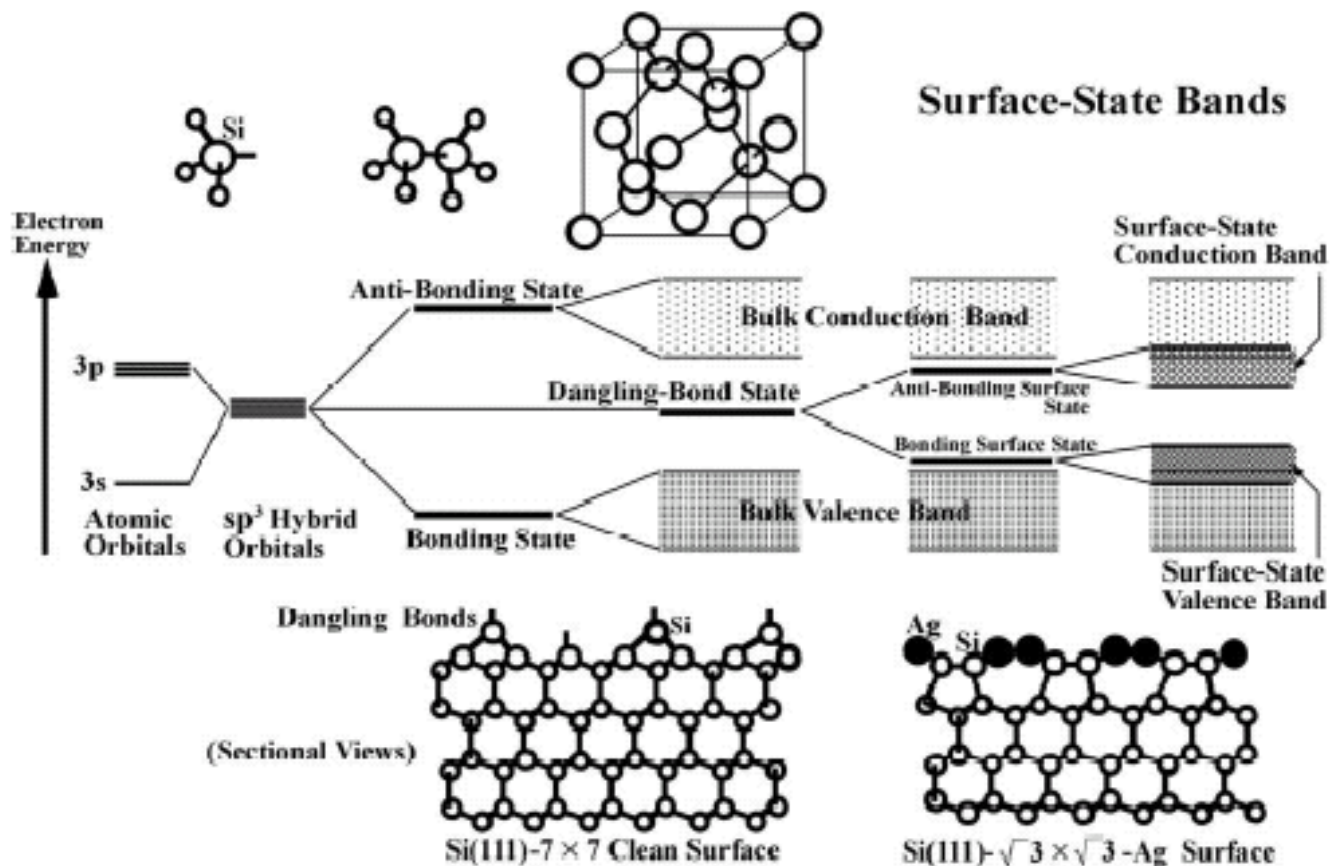


Fig. 6. A schematic illustration of energy diagram of atoms, molecules, and also in bulk and at surface of a silicon crystal. The valence electrons of an isolated Si atom are in 3p and 3s atomic orbitals. These orbitals are 'hybridized' into  $sp^3$  orbitals when the atoms arrange in tetrahedral structures like in a diamond-lattice crystal and in  $SiH_4$  molecules. When the atoms make bonds with the neighbouring atoms, the energy level of the orbitals splits into anti-bonding and bonding states. Furthermore, in the crystal the atomic orbitals overlap with each other between the neighbouring sites, the energy levels broaden into bands, conduction band and valence band, between which an energy gap opens. This is an electronic state in the bulk crystal of Si. The Si atoms on the topmost surface layer of the crystal, however, have dangling bonds, of which energy level is similar to the unpaired  $sp^3$  hybrid orbitals, locating within the band gap. The dangling-bond state split into anti-bonding and bonding states when foreign atoms bond to the topmost Si atoms. These states are created only in the surface layer, surface electronic states. When the adsorbate adsorption induces a surface superstructure, the surface states become bands due to the overlap of surface states among the periodic atomic sites on the surface. These are surface-state bands. They have characters different from the bands in the bulk crystal because the atoms in the surface superstructure arrange in a way completely different from in the bulk crystal.



## Surface density of states and band bending

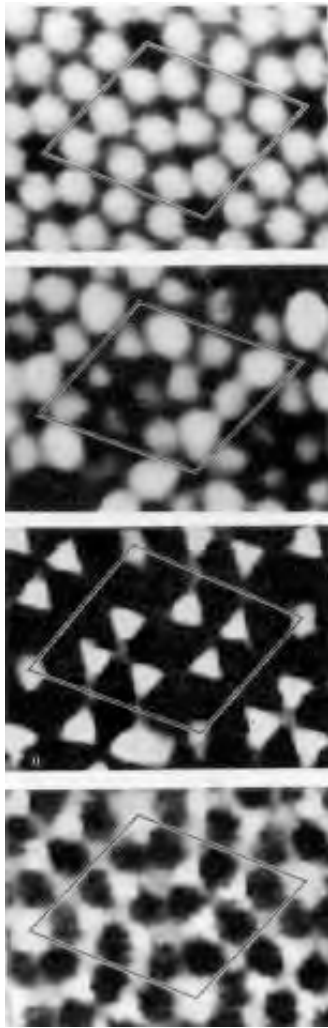
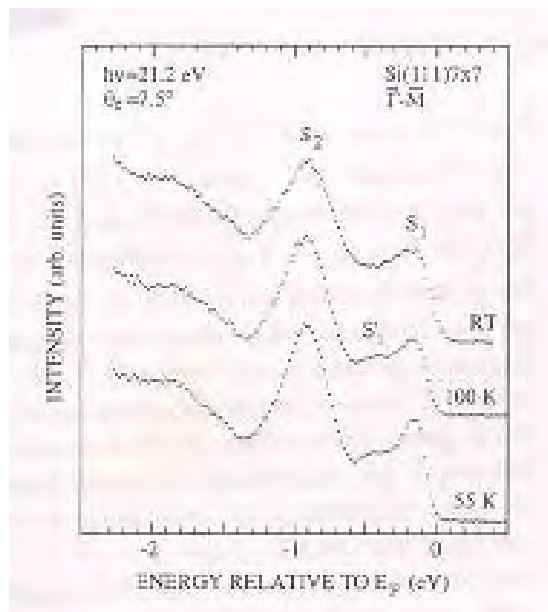


Fig. 7 Difference STM images of occupied surface states on a Si(111)7x7 surface: a) topographic image; b) adatom states at -0.35 eV; c) dangling bond states at -0.8 eV; d) back bond states at -1.7 eV [15].

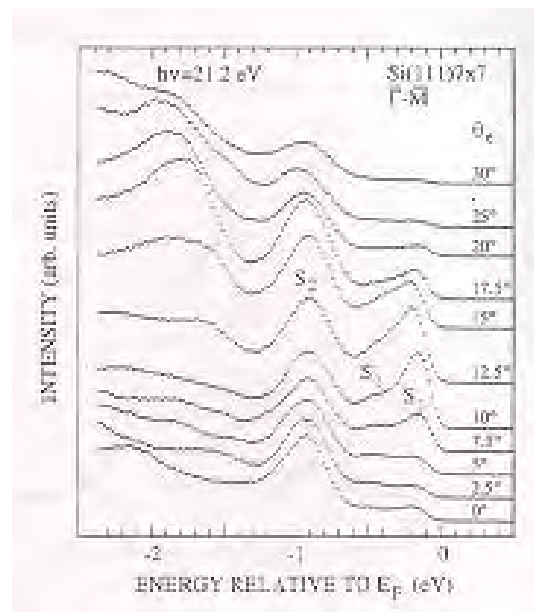
- a) Electronic properties of Si(111)7x7 surface have been analyzed using different techniques: photoemission [10], [11]; electron energy-loss spectroscopies [12],[13]; scanning tunneling microscopy [14],[15].
- b) Angle-resolved photoemission studies have consistently reported the **existence of three surface-state bands**. The two bands closest to the Fermi level  $E_F$  ( $S_1$  and  $S_2$ ) are interpreted as dangling-bond and the third is associated with back-bonds.
- c) The  $S_1$  and  $S_2$  bands show only a weak dispersion [10]. This has been verified in STM studies [15]. The  $S_1$  state, at -0.35 eV (relative to  $E_F$ ), is located on adatoms and  $S_2$ , at -0.8 eV, is located to the rest atom positions and at the corner-hole atoms. Photoemission shows significant emission at  $E_F$  implying that Si(111)7x7 surface is metallic.
- d) Low-temperature (55K) photoemission study [11] shows a previously undetected surface-state structure ( $S'_1$ ) at ~0.5 eV below  $E_F$ . It is assigned to dangling-bond states located mainly at the adatoms near the corner holes.

See next slide for results

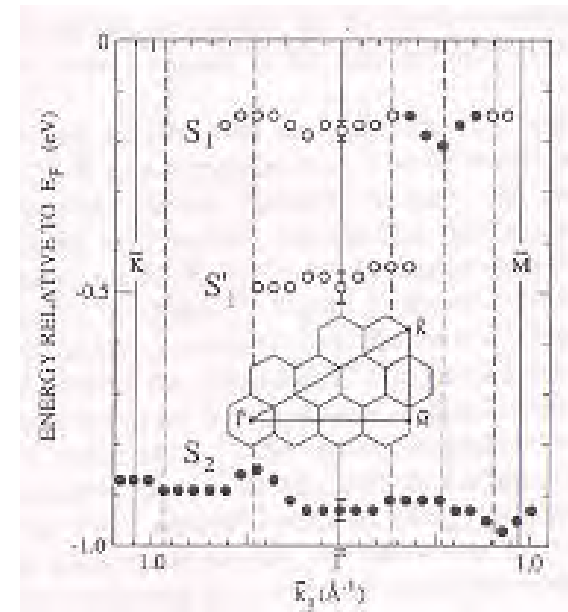


Angle-resolved spectra obtained from the Si(111)7x7 surface at three different sample temperatures.

The new surface state  $S'_1$  appears in the low- temperature spectra at  $\sim 0.5$  eV below EF [11].

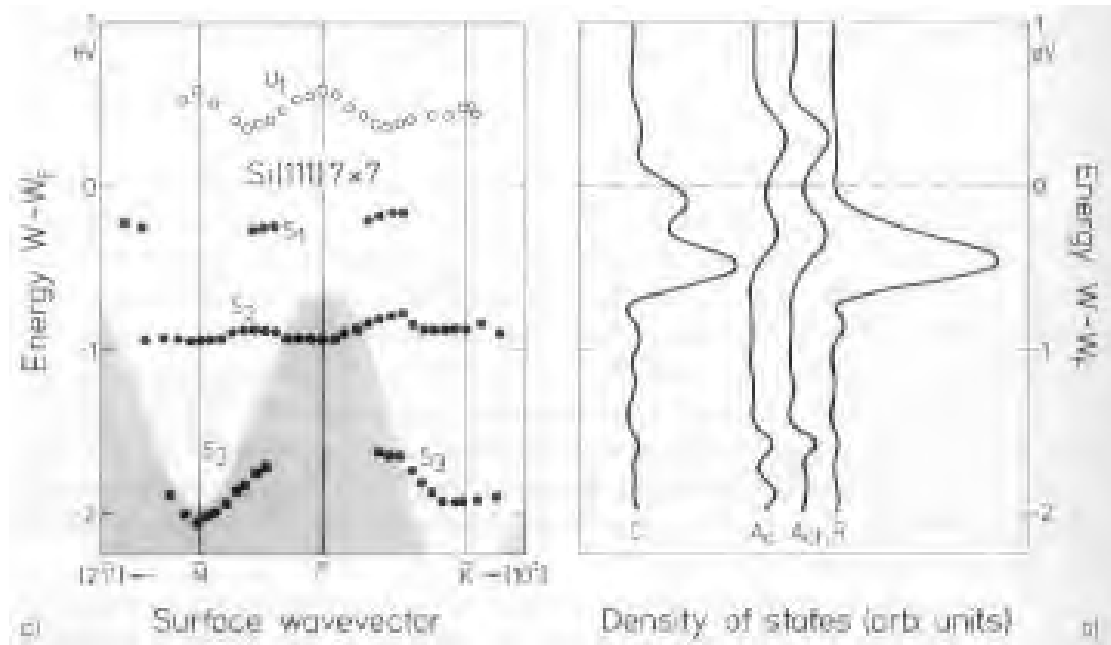


Photoemission spectra obtained for various emission angles along  $\Gamma$ -M direction of the 1x1 surface Brillouin zone (SBZ) [11].



Dispersion of the  $S_1$ ,  $S'_1$  and  $S_2$  surface states along the  $\Gamma$ -K and  $\Gamma$ -M symmetry lines of the 1x1 SBZ [11].

10. Martensson, P., Ni, W.-X., Hansson, G.V., Nicholls, J.M. and Riehl, B., Phys. Rev. B 36, 5974 (1987).
11. Uhrberg, R.I.G., Kaurila, T., Chao, Y.-C., "Low-temperature photoemission study of the surface electronic structure of Si(111)7x7", Phys. Rev. B 58, R1731 (1998)
12. Demuth, J.E., Persson, B.N.J. and Schell-Sorokin, A.J., Phys. Rev. Lett. 51, 2214 (1983).
13. Demuth, J.E., Persson, B.N.J. and Schell-Sorokin, A.J., Phys. Rev. B 30, 5968 (1984).
14. Wolkow, R. and Avouris, Ph., Phys. Rev. Lett. 60, 1049 (1988).
15. Hamers, R.J., Tromp, R.M. and Demuth, J.E., Surf. Sci. 181, 346 (1987).



Dispersion of surface states on Si(111)7x7 surfaces.

$S_1$  to  $S_4$  data for occupied states from [10] and  $U_1$  data for empty states from [16].

Shaded areas indicate surface-projected bulk valance bands:

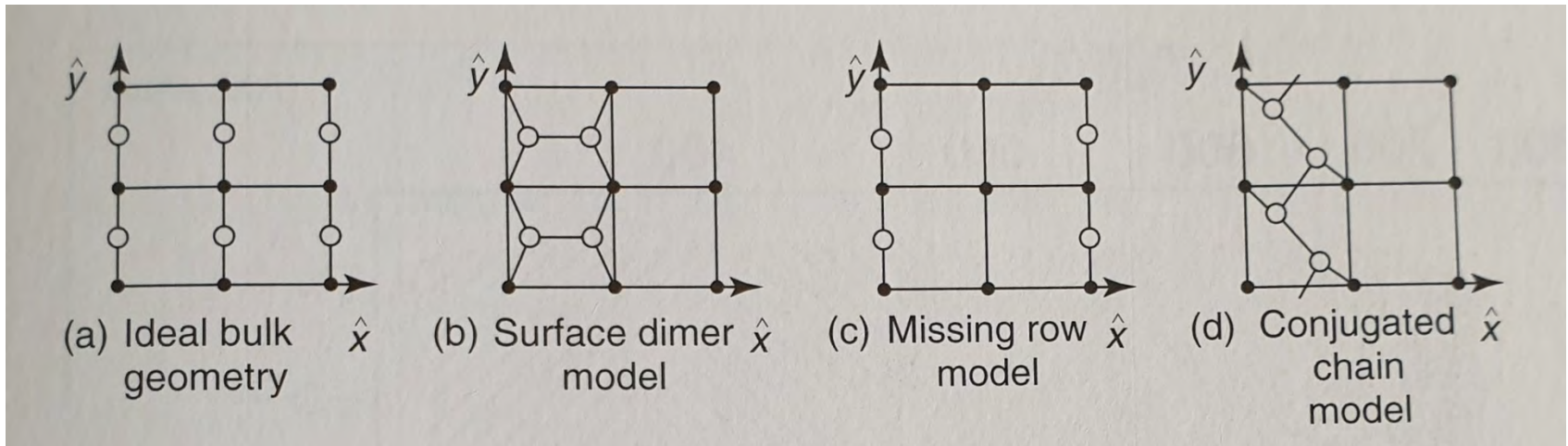
b) Local density of states of rest atoms ( $R$ ), at adatoms near to the corner holes ( $A_{ch}$ ) and in the center of the unit mesh ( $A_c$ ) as well as at corner-hole atoms  $C$  of the Si(111)7x7 DAS structure [17].

16. Nicholls, J.M. and Reihl, B., Phys. Rev. B 36, 8071 (1987).

17. Brommer, K.D., Galvan, M., Dal Pino, A. and Joannopoulos, J.D., Surf. Sci. 314, 57 (1994).



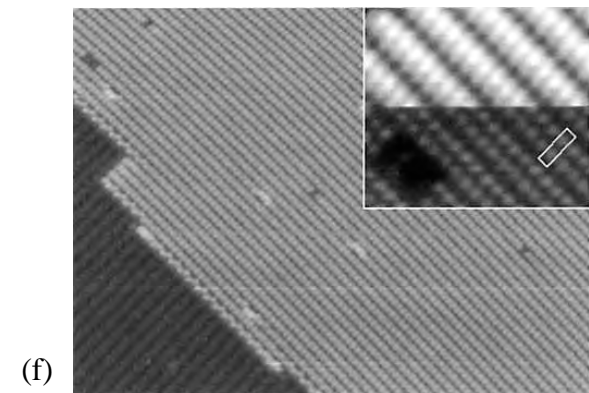
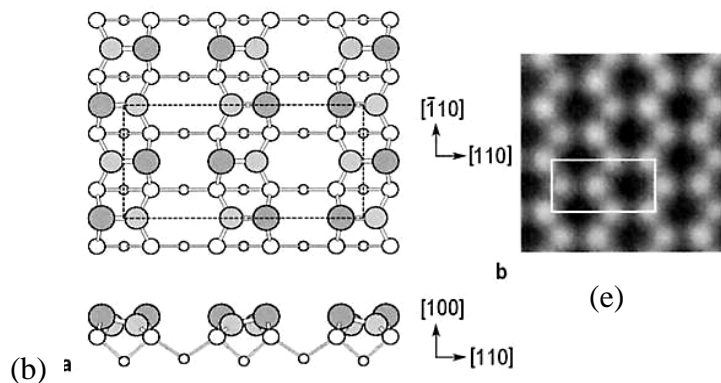
**Si(100)** - Of more practical concern because is the preferred wafer surface in device technology!



This surface exhibits a (2X1) reconstruction. In this case, several alternative structures have been proposed to account for its periodicity. The ideal bulk-terminated surface geometry (a); along with 3 alternative models with the same (2X1) periodicity: (b) Surface dimer model, (c) Missing row and conjugated chain (d).

(e) STM confirms the presence of surface dimers on this surface supporting the surface dimer model.

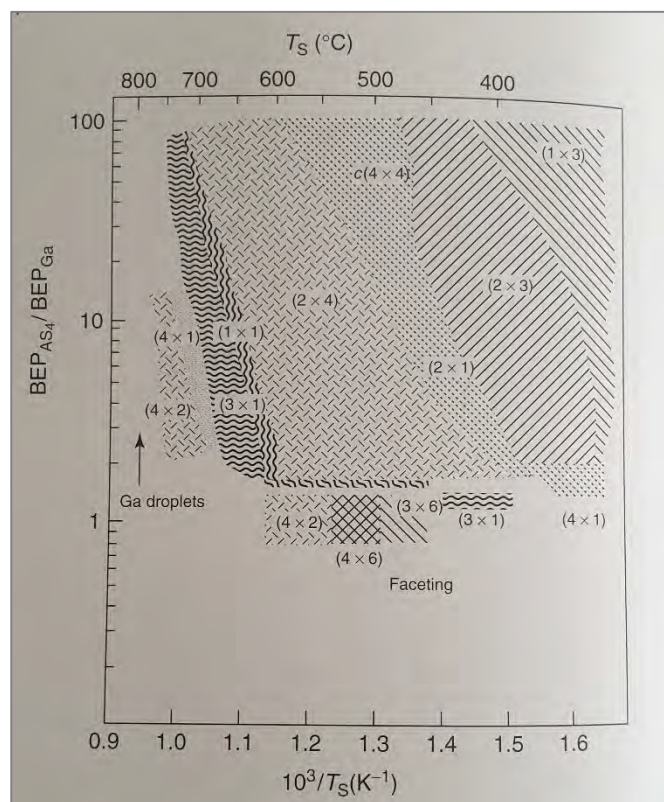
(f) These dimers are additionally buckled by  $18^\circ$  which finally leads to a c(4x2) superstructure



## Reconstructions of Compound semiconductors – Ex: Ga As (III-V compound semiconductor)

Compound semiconductors add another level of complexity since their stoichiometry can change with growth and processing as well as with crystal orientation.

The surface reconstruction of II-V compound semiconductors are of particular importance since they are used in many device applications. GaAs(100) is used more widely than any other in crystal growth and heteroepitaxy. A wide array of surface reconstructions on this surface depend on how they are grown and processed.



### Case 1: MBE growth of GaAs

The figure is a composition-temperature phase diagram, with surface phase plotted for a given composition and temperature. Phase reconstruction is measured by High Energy electron diffraction (RHEED).

The figure shows the various reconstructions reported for GaAs (100) as a function of As-to-Ga vapour flux ratio also called beam equivalent pressure (BEP), and substrate temperature during **molecular beam epitaxy (MBE) growth**.

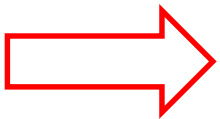
This surface phase diagram indicates that bulk growth conditions affect the surface reconstruction. Direct measurement of the surface elemental compositions demonstrates that the surface reconstruction also depends on surface stoichiometry.

### Case 2: GaAs growth by annealing

GaAs can also be grown by **annealing in As vapour** or in **vacuum** then cooling to room temperature.

In this case it is possible to change the surface reconstruction by changing the surface composition but **there is no correlation between reconstruction and composition.**

This limited correlation may be due to either (i) a **composite of multiple reconstructions** or (ii) a **structure that is more complex than an extension of primitive unit cells.**



Same situations can be reported for II-VI semiconductor compounds!

Next Lecture

Heterojunctions

Heterostructures

+

When

nano structures

become

quantum confined!