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# ATOMIC AND ELECTRONIC STRUCTURE OF SOLID SURFACES

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## ABSTRACT

**The atomic and electronic structure of solid surfaces is reviewed. Only clean and flat surfaces are considered. The main features of the surface unit cell are highlighted. The nature and types of surface reconstructions are treated. The energy structure and energetics of surfaces are also treated. An important semiconductor surface, i.e. silicon surface is discussed in the light of it's atomic structure and energetics.**

***Keywords:*** Solid surfaces, atomic structure, electronic structure, surface relaxation, surface reconstruction, surface energetics.

## INTRODUCTION

The purpose of this review is to provide a basic introduction to the physical properties and electronic structures of the important and interesting world of surfaces. On the basis that one must understand clean surfaces before one can understand how they interact with their environment this review is limited entirely to clean surfaces. In addition, the surfaces we discuss will be flat and defect free; vibrations or any other dynamic properties will not be considered; more often than not the electrons we discuss will be sitting happily in their ground state. Also, magnetic and relativistic effects will largely be ignored. Setting this list of exclusions aside, there remains much to be said about the physical properties and electronic structures of surfaces.

The surface energy and interlayer spacings of solid surfaces are important physical properties which play a role in determining the behaviour of solid surfaces when used in various applications (Desjonqueres & Spajaard, 1998; Galanakis et al, 2002). However, the direct experimental measurements of the surface energy are difficult to perform and subject to various uncertainties, e.g., presence of impurities. In addition, most of the available experimental surface-energy data of solids are obtained from surface tension measurements in the liquid phase and extrapolated to zero temperature, which does not provide the orientation dependence of the surface energy (Da Silva et al, 2006). Due to the difficulties in obtaining experimental surface energies, as well as their orientation dependence, accurate calculations based on density functional theory (DFT) methods play an important role (Giannozzi, 2005; Baer, 2008; Kohanoff, 2006; Martin, 2004).

There are two approaches by which to obtain surface energies from DFT calculations: (i) one may evaluate the total energy of a slab of the particular solid and subtract the corresponding bulk total energy obtained from a separate calculation. Alternatively, (ii), one may use slabs of different thicknesses and extract from them the bulk energy (Da Silva et al, 2006). It has been argued by Boettger (1994), Boettger et al (1998), and Fiorentini & Methfessel (1996) that approach (i) is problematic, yielding surface energies that diverge linearly as a function of the slab thickness. The origin of this problem is that often slab and bulk total energies are calculated with different levels of accuracy. Thus, Fiorentini & Methfessel suggested that approach (ii) is superior: extracting the bulk total energy from the slope of the slab total energy versus the number of layers in the slab ensures that surface and bulk are extracted with the same accuracy.

Experimentally, the best accessible surface property is the atomic structure, i.e., the interlayer relaxations. The atomic structure can be obtained with high accuracy using quantitative low-energy electron diffraction (LEED) intensity analysis (Bhadeshia, 2001; Galperin, 2002; Mihaly & Martin, 1996; Hammond, 2001). And theoretically, first-principles DFT calculations also give an accurate description. It has been found that the majority of transition metal surfaces show a contraction of the first interlayer spacing, i.e., the spacing between the two outermost layers is smaller than in the bulk terminated (unrelaxed) surface (Oura et al, 2003; Nix, 2003; Venables, 2010).

## MATERIALS AND METHODS

### ATOMIC COMPOSITION OF SURFACES AND INTERFACES

A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state. There are mainly three phases of matter namely solid, liquid and gas. The word fluid is used to describe both gas and liquid phases. We usually classify the phase of a material according to its state at the normal ambient temperature (20–25°C), which is well above the boiling point of most fluids. We mostly deal with two or more phases, which coexist, in equilibrium or non-equilibrium conditions. Phase diagrams are used as a convenient method of representing the regions of stability of solid, liquid and gas phases under various conditions of temperature and pressure.

An interface is the physical boundary between two adjacent bulk phases. The interface must be at least one molecular diameter in thickness for the purpose of constructing a molecular model. In some cases it may extend over several molecular thicknesses. We use the word surface in order to define the physical boundary of only one of these phases, such as solid surface and liquid surface, etc (Duxbury & Pence, 2002; Riviere & Myhra, 2009). In reality, we deal with an interface in all cases other than absolute vacuum conditions for solids, since every single phase is in contact with another phase such as solid–air, liquid–air contacts, etc.

The quantitative understanding of bulk solids on an atomic level is greatly simplified by the periodic structure of crystalline matter since the periodicity reduces the electronic and nuclear degrees of freedom from 1023 per cm3 to the degrees of freedom in a single unit cell (Fletcher, 1971). However, at surfaces the reduction in the degrees of freedom by periodicity is less, as the three-dimensional symmetry is broken (Altland & Simons, 2001; Brune et al, 1997). Therefore, near surfaces, material properties may differ from the bulk in several monolayers below the surface. Frequently, the unit cell of a real surface is substantially larger than the surface unit cell of a terminated bulk, which increases the number of atoms in the surface unit cell. For example, the surface cell of the clean (111) surface of silicon contains 49 atoms in one atom layer (Da Silva et al, 2006).

### Atomic Structure of Surface

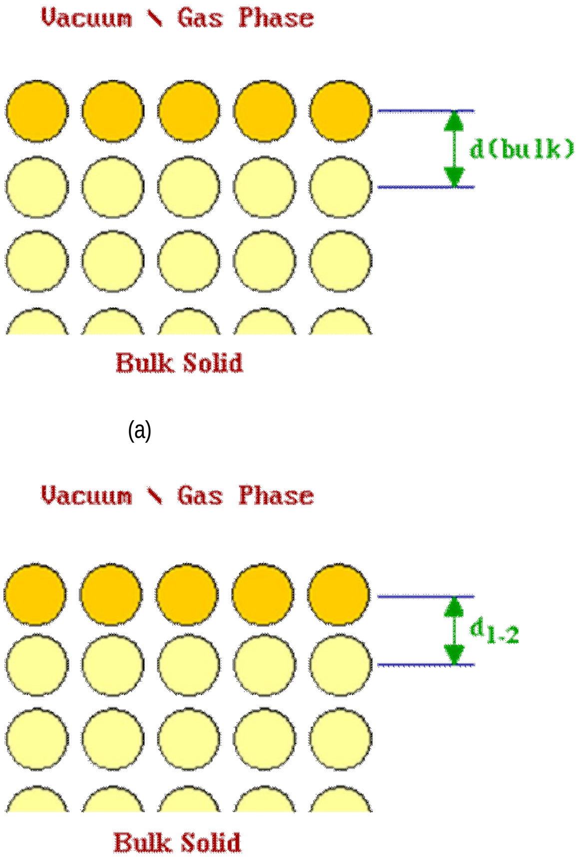
When a crystal is cut along some orientation, the atoms located in the few outer layers experience non-zero forces which are induced by the breaking of bonds. The bond-breaking process in the surface formation induces forces which push the outer layer atoms out of their bulk positions. Since energy is required to break these bonds, the most stable surfaces are those with the smallest number of broken bonds. They are also the most compact surfaces on which the coordination number of the atoms is not greatly reduced. The breaking of bonds may also produce point or extended defects, as well as lattice distortions (Ibach, 2006). When a two-dimensional periodicity is kept in the surface layers, the structural distortions are called relaxations, rumpling or reconstructions. A feature common to all structural distortions is the lowering of surface energy (Noguera, 1996). This must be taken into account when comparing the stability of different faces of a given material.

A plane in a crystal is identified by three integers (h,k,l), called the Miller indices. These integers are in the same ratio as (1/x, 1/y, 1/z), the reciprocals of the coordinates of the intercepts of this plane with the axes of the unit cell of the crystal (Kittel, 1996; Galperin, 2002;). Notations with four indexes (h, k, -(h+k),l) are used in hexagonal structures, such as α-quartz, corundum α-alumina, or the wurtzite ZnO structure (The Wikipedia, 2009). If several planes, e.g. the (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$, (001) and $(00\bar{1})$ planes in a cubic crystal, are structurally equivalent, such collection is denoted by one of the planes in curly brackets. Low-index surfaces are more compact and generally more stable than high-index surfaces (Oura et al, 2003).

For strictly two-dimensional periodic structures, there exist five Bravais lattices: square, rectangular, centred rectangular, hexagonal and oblique (Kittel, 1996; Galperin, 2002). However, real surfaces rarely present a perfect ordering. Depending upon the conditions under which they are prepared – cutting, polishing, etc, - various defects may be found: steps with ledges and terraces, kinks, ad-atoms, ad-vacancies, etc (Ibach, 2006).

## Surface Relaxation

Surface relaxation is the change in the spacing between the surface top layer and the underlying plane.It is as a result of small and subtle rearrangement of the surface layers which is significant energetically. It is commonplace for metal surfaces. It involves adjustments in the layer spacings perpendicular to the surface, but with no change either in the periodicity parallel to the surface or to the symmetry of the surface (Noguera, 1996; Nix, 2003). An inward relaxation corresponds to a spacing contraction while an outward relaxation corresponds to a spacing expansion. Relaxation effects are mostly pronounced in the first layer but may affect several layers to a lesser degree.



(a)

(b)

Fig. 1: (a) Unrelaxed surface of a solid (b) Relaxed surface of a solid [Source: Nix, 2003]

In the relaxed surface, the first layer of atoms is typically drawn in slightly towards the second layer (i.e. d1-2 < dbulk ). If we use a localised model for the bonding in the solid then it is clear that an atom in the bulk is acted upon by a balanced, symmetrical set of forces. On the other hand, an atom at the unrelaxed surface suffers from an imbalance of forces and the surface layer of atoms may therefore be pulled in towards the second layer. The magnitude of the contraction in the first layer spacing is generally small (< 10 %) (Nix, 2003). Compensating adjustments to other layer spacings may extend several layers into the solid.

## Surface Rumpling

Layers which contain two or more types of atoms may rumple. For example, on oxide surfaces, the oxygen anions and the cations move in opposite vertical directions. The anions are generally displaced outwards and the cations inwards. This effect is also found on ZnS {110} surfaces. Rumpling and relaxations effects often occur simultaneously. The surface structure is better described as the result of anion and cation relaxations having different strengths (Noguera, 1996).

## Surface Reconstruction

The reconstruction of surfaces is a much more readily observable effect than relaxation, involving larger displacements of the surface atoms. It occurs with many of the less stable metal surfaces, e.g. it is frequently observed on fcc (110) surfaces, but is much more prevalent on semiconductor surfaces (Da Silva et al, 2006).

Unlike relaxation, the phenomenon of reconstruction involves a change in the periodicity of the surface structure. The diagram below shows a surface, viewed from the side, which corresponds to an unreconstructed termination of the bulk structure (Nix, 2003).

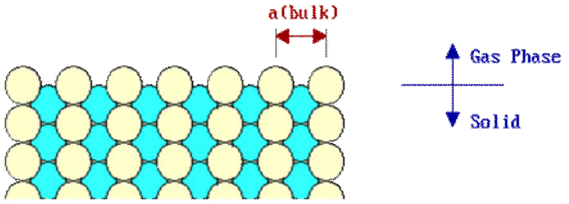


Fig. 2: Unreconstructed Surface [Source: Nix, 2003].

This may be contrasted with the following picture which shows a schematic of a reconstructed surface. This particular example is similar to the "missing row model" proposed for the structure of a number of reconstructed (110) fcc metal surfaces (Nix, 2003).

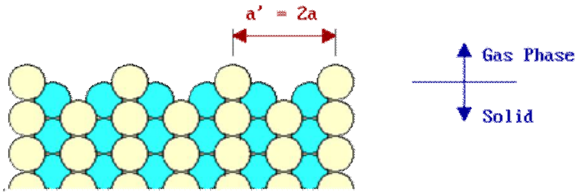


Fig. 3: Reconstructed Surface [Source: Nix, 2003].

Since reconstruction involves a change in the periodicity of the surface and in some cases also a change in surface symmetry, it is readily detected using surface diffraction techniques like LEED (Brommer, 1992; Chadi, 1979).

The overall driving force for reconstruction is the minimization of the surface free energy. At the atomic level, however, it is not always clear why the reconstruction should reduce the surface free energy. For some metallic surfaces, it may be that the change in periodicity of the surface induces a splitting in surface-localized bands of energy levels and that this can lead to a lowering of the total electronic energy when the band is initially only partly full (Binnig, 1983).

In the case of many semiconductors, the simple reconstructions can often be explained in terms of a "surface healing" process in which the co-coordinative unsaturation of the surface atoms is reduced by bond formation between adjacent atoms (Korvink and Greiner, 2002). For example, the formation of a Si (100) surface requires that the bonds between the Si atoms that form the new surface layer and those that were in the layer immediately above in the solid are broken - this leaves two "dangling bonds" per surface Si atom (Nix, 2003).

A relatively small co-ordinated movement of the atoms in the topmost layer can reduce this unsatisfied co-ordination - pairs of Si atoms come together to form surface "Si dimers", leaving only one dangling bond per Si atom. This process leads to a change in the surface periodicity: the period of the surface structure is doubled in one direction giving rise to the so-called (2 x 1) reconstruction observed on all clean Si(100) surface (Shi et al, 2002 and Chadi, 1979). So far, we have concentrated on the reconstruction of clean surfaces. It is, however, worth noting that reconstruction of the substrate surface is frequently induced by the adsorption of molecular or atomic species onto the surface - this phenomenon is known as adsorbate-induced reconstruction (Drabol and Estreicher, 2007).

In general, the change in a surface layer's structure due to a reconstruction can be completely specified by a matrix notation proposed by Park and Madden (Oura et al, 2003). If a and b are the basic translation vectors of the two-dimensional structure in the bulk and as and bs are the basic translation vectors of the superstructure or reconstructed plane, then the relationship between the two sets of vectors can be described by the following equations:

$$\mathbf{a_s} = G_{11}\mathbf{a} + G_{12}\mathbf{b} \qquad 1.0$$

$$\mathbf{b_s} = G_{21}\mathbf{a} + G_{22}\mathbf{b} \qquad 2.0$$

so that the two-dimensional reconstruction can be described by the matrix

$$G = \begin{pmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{pmatrix} \qquad 3.0$$

Note that this system does not describe any relaxation of the surface layers relative to the bulk inter-layer spacing, but only describes the change in the individual layer's structure.
Surface reconstructions are more commonly given in Wood's notation, which reduces the matrix above into a more compact notation (Ibach, 2006):

$$X(hkl)\ m \times n\ R\varphi \qquad 4.0$$

which describes the reconstruction of the (hkl) plane (given by its Miller indices) into one in which the interatomic spacings are multiplied by m and n in the a and b directions respectively, and rotated by the angle phi. This notation is often used to describe reconstructions concisely, but does not directly indicate changes in the layer symmetry, for example, square to hexagonal.

## SURFACE ENERGETICS

The energy to make a surface at a given temperature and pressure is the Gibb's surface free energy, Gs, which is defined by the relation (Desjonqueres and Spanjaard, 1998)

$$G = NG^0 + AG^s, \qquad 5.0$$

where G is the total free energy of the solid, N is the number of atoms in the solid, G0 is the free energy per atom in the infinite solid, and A = surface area. The Gibb's free energy is usually different for different facets (orientations) of a crystal. Such variations, referred to as surface free energy anisotropies, are key to determining the equilibrium crystal shape of materials because at equilibrium a crystal seeks to minimize its total surface free energy subject to the constraint of constant volume.
Because of the difficulty in acquiring reliable surface free energies of solids, when dealing with one component systems, it is common to exploit the equivalence of Gs and surface tension, γ (Somorjai, 1994). The surface tension, particularly the surface tension of liquids, can be determined more accurately than Gs for solids. It is generally believed that the surface tension of a molten liquid is about 10-20 % less than Gs for the close-packed surfaces of that solid. Thus liquid surface tension measurements provide an average surface free energy of the low index solid surfaces. Generally these values are extrapolated on semi-theoretical grounds to 0 K (Lide, 1995; Miller & Tyson, 1977).
All surfaces are energetically unfavourable in the sense that they have a positive free energy of formation (Kittel, 1996; Venables, 2010). A simple rationalisation for this is that in the formation of new surfaces by cleavage of a solid, bonds have to be broken between atoms on either side of the cleavage plane in order to split the solid and create the surfaces. Breaking bonds requires work to be done on the system, so the surface free energy (surface tension) contribution to the total free energy of a system must therefore be positive. The unfavourable contribution to the total free energy may be minimised in several ways:
i. by reducing the amount of surface area exposed (reconstruction),
ii. by predominantly exposing surface planes which have a low surface free energy,
iii. by altering the local surface atomic geometry in a way which reduces the surface free energy (relaxation).

There is a direct correspondence between the concepts of "surface stability" and "surface free energy" i.e. surfaces of low surface free energy will be more stable and vice versa. The most stable solid surfaces are those with a high surface atom density and having surface atoms of high coordination number (Stampfl, et al, 2006). For example, if we consider the individual surface planes of an fcc solid, then we would expect the stability to decrease in the order fcc (111) > fcc (100) > fcc (110). This is strictly the case when the surfaces are in vacuum. The presence of a fluid above the surface (gas or liquid) can drastically affect the surface free energies as a result of the possibility of molecular adsorption onto the surface. Preferential adsorption onto one or more of the surface planes can significantly alter the relative stabilities of different planes. The influence of such effects under reactive conditions (e.g. the high pressure/high temperature conditions pertaining in heterogeneous catalysis) is poorly understood (Yu, et al, 2006).

### Theoretical Calculations of Surface Energies

In theoretical calculations, such as DFT, the T=0 value of Gs is typically calculated. In terms of a periodic slab calculation the surface energy, Es, is more conveniently defined with regard to surface area as

$$G^s \sim E^s = \frac{E_{tot}^{slab} - NE_{tot}^{bulk}}{2A} \qquad 6.0$$

where

$E_{tot}^{slab}$= total energy of a slab with N atoms and

$E_{tot}^{bulk}$= reference total energy per atom of the bulk system.

The factor ½ takes into account the presence of two equivalent surfaces of the slab. To obtain $E^s$ one needs to compute just two quantities, $E_{tot}^{slab}$and $E_{tot}^{bulk}$ (Da Silva *et al*, 2006).

Surface free energy is proportional to the number of broken bonds at the surface. Bonds between an atom with a few neighbours are stronger than those between an atom with many neighbours. This coordination number bond strength has been calculated explicitly with DFT for several solids showing that the energy per bond can be as much as twice as large for C=2 compared to C=12 (Methfessel *et al*, 1992; Heine *et al*, 1991).

**Surface Energies and Cohesive Energies**

The surface energy of any element is a fraction of its cohesive energy, $E^{coh}$. Most often it turns out that for metals $G^s$ per surface atom is approximately 1/6$E^{coh}$ per bulk atom (Overbury *et al*, 1975). The coordination number bond strength relationship is qualitatively captured in simple tight binding schemes in which the energy per bond can be assumed to scale with $\sqrt{C}$ leading to

$$E^s = \frac{\left(\sqrt{C^{bulk}} - \sqrt{C^{surf}}\right)E^{coh}}{\sqrt{C^{bulk}}} \qquad 7.0$$

where $C^{bulk}$ is the bulk atom coordination number, and $C^{surf}$ is the surface atom coordination number.

Because of the difficulty in acquiring reliable surface free energies of solids, when dealing with one component systems, it is common to exploit the equivalence of $G^s$ and surface tension, γ (Somorjai, 1994). The surface tension, particularly the surface tension of liquids, can be determined more accurately than $G^s$ for solids. It is generally believed that the surface tension of a molten liquid is about 10-20 % less than $G^s$ for the close-packed surfaces of that solid. Thus liquid surface tension measurements provide an average surface free energy of the low index solid surfaces. Generally these values are extrapolated on semi-theoretical grounds to 0 K (Lide, 1995; Miller & Tyson, 1977).

## SILICON SURFACES

Silicon is a semiconductor widely used in a variety of computing and microelectronics applications. It has been and will most probably continue to be the dominant material in semiconductor technology (Korvink & Greiner, 2002). The bulk Silicon has a diamond-like face-centred cubic (fcc) lattice and exhibits several different well-ordered reconstructions depending on temperature and on which crystal face is exposed. For example, when Si is cleaved along the (100) surface, the ideal diamond-like structure is interrupted and results in a 1 x 1 square array of surface Si atoms. Each of these has two dangling bonds remaining from the diamond structure, creating a surface which can obviously be reconstructed into a lower-energy structure. The observed reconstruction is a 2 x 1 periodicity, explained by the formation of dimers which consist of paired surface atoms, decreasing the number of dangling bonds by a factor of two. These dimers reconstruct in rows with a high long-range order, resulting in a surface of filled and empty rows (Hammond, 2001). LEED studies and calculations also indicate that relaxations as deep as five layers into the bulk are also likely to occur (Binnig, 1983; Brommer, 1992; Chadi, 1979).

The Si (111) structure, by comparison, exhibits a much more complex reconstruction. Cleavage along the (111) surface at low-temperatures results in another 2 x 1 reconstruction, differing from the (100) surface by forming long pi-bonded chains in the first and second surface layers. However, when heated above 400 $^{o}$C this structure converts irreversibly to the more complicated 7 x 7 reconstruction. In addition, a disordered 1 x 1 structure is regained at temperatures above 850 $^{o}$C which can be converted back to the 7 x 7 reconstruction by slow cooling (Binnig, 1983; Brommer, 1992; Chadi, 1979).

The 7 x 7 reconstruction is modelled according to a dimer-adatom-stacking fault (DAS) model which was constructed by many research groups (Brommer, 1992). Extending through the five top layers of the surface, the unit cell of the reconstruction contains 12 adatoms as well as two triangular subunits, nine dimers and a deep corner hole which extends to the fourth and fifth layers (Brommer, 1992). This structure was initially inferred from LEED measurements as well as calculation, and was finally resolved in real space as a demonstration of the STM which was developed by Binnig and Rohrer at IBM's Zurich Research Laboratory. The full structure with positions of all reconstructed atoms has also been confirmed by massively parallel computation (Binnig, 1983).

A number of similar DAS reconstructions have also been observed on Si (111) in non-equilibrium conditions in a (2n+1) x (2n+1) pattern, and include 3 x 3, 5 x 5 and 9 x 9 reconstructions. The preference for the 7 x 7 reconstruction is attributed to an optimal balance of charge transfer and stress, but the other DAS-type reconstructions can be obtained under conditions such as rapid quenching from the disordered 1 x 1 structure (Brommer, 1992, Binnig, 1983).

## CONCLUSION

An interface is the physical boundary between two adjacent bulk phases. The interface must be at least one molecular diameter in thickness for the purpose of constructing a molecular model. In some cases it may extend over several molecular thicknesses. We use the word surface in order to define the physical boundary of only one of these phases, such as solid surface and liquid surface, etc (Duxbury & Pence, 2002; Riviere & Myhra, 2009). In reality, we deal with an interface in all cases other than absolute vacuum conditions for solids, since every single phase is in contact with another phase such as solid–air, liquid–air contacts, etc.

The quantitative understanding of bulk solids on an atomic level is greatly simplified by the periodic structure of crystalline matter since the periodicity reduces the electronic and nuclear degrees of freedom from $10^{23}$ per $cm^3$ to the degrees of freedom in a single unit cell (Fletcher, 1971). However, at surfaces the reduction in the degrees of freedom by periodicity is less, as the three-dimensional symmetry is broken (Altland & Simons, 2001; Brune et al, 1997). Therefore, near surfaces, material properties may differ from the bulk in several monolayers below the surface. Frequently, the unit cell of a real surface is substantially larger than the surface unit cell of a terminated bulk, which increases the number of atoms in the surface unit cell. For example, the surface cell of the clean (111) surface of silicon contains 49 atoms in one atom layer (Da Silva et al, 2006).

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