

# Physics of Low Dimensional Systems

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## 1 Surface Thermodynamics

It is not reasonable to think the surface as a geometrical plane since surface effects characterize many layers. Let us consider a crystal composed of one element. This system is in equilibrium with the environment and we can plot the density in function of the perpendicular axis:

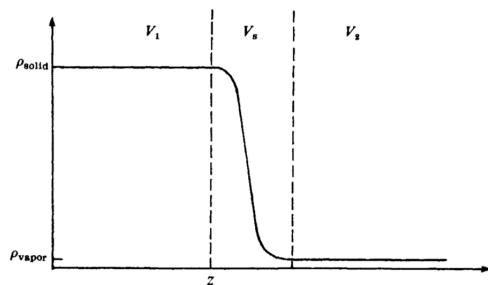


Figure 1: One component density

Now we can ask ourselves where is the surface. It is possible to set the dividing plane such that from a thermodynamic point of view we can define the bulk and then add something more related to the specific surface. It is possible to find the dividing plane position where the surface excess is compensated:

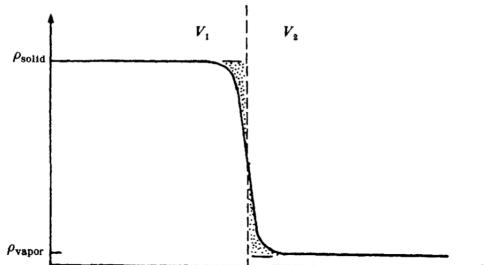


Figure 2: Dividing plane and equal areas

In thermodynamics there are several potential. The first one is the internal energy:

$$U = U(S, V, N)$$

$$dU = TdS - pdV + \mu dN$$

which depends on the extensive variables entropy, volume and number of particles. Using the Legendre transformation we can obtain the Helmholtz free energy:

$$F = U - TS$$

Therefore we can differentiate its:

$$dF = dU - TdS - SdT = TdS - pdV + \mu dN - TdS - SdT$$

and

$$dF = -SdT - pdV + \mu dN$$

We have obtained that the Helmholtz free energy depends on the temperature, the volume and the number of particles:

$$F = F(T, V, N)$$

With the same procedure we can write the Gibbs free energy:

$$G = F + pV$$

$$dG = dF + pdV + Vdp = -SdT + Vdp + \mu dN$$

and therefore:

$$G = G(T, p, N)$$

The last potential we introduce is the Landau potential:

$$\Omega = F - \mu N$$

$$d\Omega = -SdT + pdV - Nd\mu$$

and therefore:

$$\Omega = \Omega(T, V, \mu)$$

Note that the Landau potential depends only on intrinsic variable. Let us introduce the Gibbs-Duhem equation:

$$Nd\mu = Vdp - SdT$$

This means that all the intrinsic variables are linked together. Another formulation of the GD equation is:

$$\sum_j n_j \mu_j = 0$$

therefore a variation in one component affects all the others. We have written the Gibbs free energy as:

$$dG = -SdT + Vdp + \mu dN$$

$$dG = Nd\mu + \mu dN = d(\mu N)$$

We can conclude that:

$$G = \mu N$$

From the previous considerations:

$$\Omega = F - \mu N = F - G = -pV$$

Since the number of particles on the surface is negligible the Landau potential of the surface is equal to the Helmholtz free energy of the surface:

$$\Omega_s = F_s$$

Considering the solid and vapor phases, once we have identified the dividing plane the difference in the thermodynamic properties between the phase is considered an excess:

$$\Delta S_s = -\Delta S_1 - \Delta S_2$$

$$\Delta V_s = -\Delta V_1 - \Delta V_2$$

$$\Delta N_s = -\Delta N_1 - \Delta N_2$$

To the total energy of the system we add the excess component proportional to area with the constant  $\gamma$  defined as surface excess free energy:

$$\Omega = F - G = \Omega_b + \Omega_s = -p(V_1 - V_2) + F_s$$

$$F_s = \gamma A$$

If we consider the Langmuir-Blodgett technique for single layer deposition of controlled assembly organic molecules on liquid interface, the system is composed on a very large reservoir of  $H_2O$  molecules. This means that the free energy associated to the formation of the surface does not depend of the chemical potential:

$$\Omega_s = \Omega_s(T, A, \mu) = dW_s = \gamma dA$$

In crystals we don't have this reservoir. Moreover, we have to take in account the stress ( $\sigma_{ij}$ ) and strain ( $\epsilon_{ij}$ ) tensors. These effects can affect several layers and can change the chemical potential. In this case it is better to use the Helmholtz potential.

$$F_s = F_s(T, A, N)$$

$$dW_s = dF_s = d(\gamma' A) = Ad\gamma' + \gamma' dA$$

As we have already demonstrated:

$$F_s = \Omega_s + G_s$$

$$dF_s = d\Omega_s + dG_s = d(\gamma A) + d(\mu N)$$

$$d(\gamma A) + d(\mu N) = Ad\gamma' + \gamma' dA$$

Therefore we can say that:

$$dW_s = (\gamma + \mu \frac{dN}{dA}) \cdot dA + (d\gamma + d\mu \frac{N}{A}) \cdot A = Ad\gamma' + \gamma' dA$$

Finally if we consider multiple component systems:

$$\gamma' = \gamma + \sum_j \mu_j \Gamma_j$$

This equation is consistent with the Gibbs model. We have simply to add the surface excess of different components to the bulk (defined by the dividing plane) surface tension  $\gamma$ .

Now with a more complex approach we can derive the Shuttleworth equation:

$$\sigma_{ij} = \gamma \frac{\partial \gamma'}{\partial \epsilon_{ij}}$$

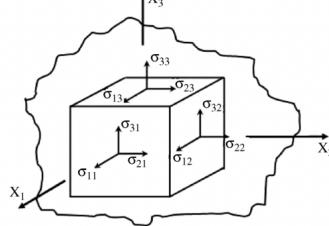


Figure 3: Action of the components  $\sigma_{ij}$  of the bulk stress tensor applied on the three front faces of an elementary cube cut in a piece of matter. Each face normal to  $x_j$  axis bears a triplet  $\sigma_{ij}$ . The first index  $i = 1; 2; 3$  gives the direction  $x_i$  where the stress acts. On the back faces of the cube, there are identical stresses of opposite sign, image from [1].

From this picture is clear that the different surface orientation of a crystal are not equivalent. A simple rough calculation of the surface tension  $\gamma(hkl)$  along a specific crystallographic axis can be done considering a vicinal surface system.

Consider the terraces composed of  $b$  unit lengths and separated  $a$  unit lengths, as shown in figure. The vicinal surface plane will have an orientation of

$$\tan(\theta) = \frac{a}{b}$$

The step density is:

$$\sigma_s = \frac{1}{b} = \frac{\tan(\theta)}{a}$$

Considering  $b = na$ :

$$\tan(\theta) = \frac{1}{n}$$

In general we want to have large Miller indices in order to avoid interaction between steps. Therefore the  $\theta$  angle is small. The surface energy of low index plane (01) is defined as  $\gamma_o$  and the steps make

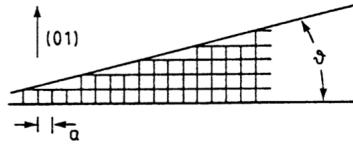


Figure 4: Vicinal surface, image from [1]

a contribution  $\beta_s$  to the total surface energy. One might express the surface energy as a series of step density  $\tan(\theta)/a$ :

$$\gamma(\theta) = \cos(\theta)\gamma_o + \beta_s \frac{\tan(\theta)}{a} \cos(\theta)$$

The Wullf plot describe the surface energy at different angles. In the case of vicinal surface, at the first order, we obtain the following plot.

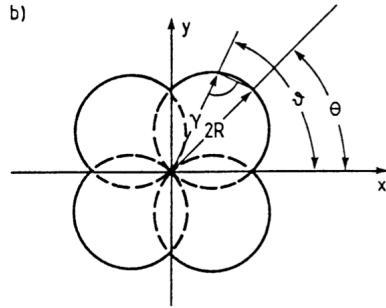


Figure 5: Wullf plot of vicinal surface, image from [1].

**Recap:** Gibbs defined thermodynamically the problem of the equilibrium shape of crystals as the shape at which the crystal has a minimum surface energy at given constant volume. This definition later acquired a geometric interpretation in the well-known Gibbs–Wulff theorem, according to which the distances  $h_n$  from an arbitrary (Wulff's) point to the different crystal faces are proportional to the corresponding specific surface energy  $\gamma_n$  of these faces:

$$\gamma_n = m \cdot h_n$$

### 1.1 Soap Bubble

Let us consider a soap bubble of radius  $R$  at constant temperature. The bubble doesn't explode therefore there is an equilibrium between the difference in pressure and the surface tension of the soap:

$$dW = pdV = (p_i - p_o)4\pi R^2 dR$$

$$dW_s = -2\gamma dS$$

In equilibrium we have that:

$$dW + dW_s = 0$$

The theory has been developed using the so called Dupre frame: We pull the frame with a

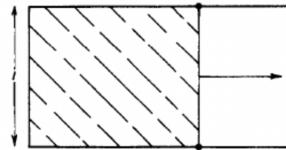


Figure 6: Dupre frame

constant force  $F$ , creating a displacement  $dh$  and an area  $dA$  for both sides:

$$Fdh = 2\gamma dA = 2\gamma L dh$$

$$\gamma = \frac{F}{2L}$$

The factor  $\gamma$  has the dimension of Newton over length and it is called surface tension. Since any direction for liquid are equal in this case the surface free energy is equal to the surface tension. In general this is not true!

Now considering that:

$$dW + dW_s = 0$$

we can rewrite the following equation (Young-Laplace eq.):

$$(p_i - p_o) \cdot 4\pi R^2 dR = 2\gamma d(4\pi R^2)$$

$$(p_i - p_o) \cdot 4\pi R^2 dR = 2\gamma 8\pi R dR$$

$$(p_i - p_o) = \frac{4}{R} \gamma$$

This means that, in order to consider the surface contribution, the inner pressure must be larger than the external pressure.

## 2 Introduction to Tight Binding for Periodic Lattice

The tight-binding approximation deals with the case in which the overlap of atomic wave functions is enough to require correction to the picture of isolated atoms, but not so much to as to render the atomic description irrelevant.

This approximation is most useful to describe energy band that arise from the partially filled d-states of transition metal atoms and for insulators.

### 2.1 General Formulation

First of all we assume that in the vicinity of lattice point, the full periodical Hamiltonian  $H$  can be approximated by the atomic Hamiltonian,  $H_{at}$ , of the single atom. We also assume that the bound levels are well localized:

$$H_{at}\psi_n = E_n\psi_n$$

Then we require that  $\psi_n(\mathbf{r})$  be very small when  $\mathbf{r}$  exceeds the lattice constant. The crystal Hamiltonian can be written as:

$$H = H_{at} + \Delta U(\mathbf{r})$$

where  $\Delta U(\mathbf{r})$  introduces the effects of periodic potential. If  $\psi_n$  satisfies the atomic Schrodinger equation then it will also satisfies the crystal Schrodinger equation since  $\Delta U(\mathbf{r})$  vanishes wherever  $\psi_n$  does not. If this were the case, then each atomic level  $\psi_n(\mathbf{r})$  would yield N levels in the periodic potential, with wave function  $\psi_n(\mathbf{r} - \mathbf{R})$ , for each of the N side  $\mathbf{R}$  in the lattice. To preserve the Bloch description we must find the N linear combination of wave function that satisfy the Bloch condition:

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r})$$

The linear combination is:

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\psi(\mathbf{r} - \mathbf{R})$$

Note we stated that  $\psi_n(\mathbf{r})$  is simply the atomic stationary state. This assumption is not really valid since  $\psi_n(\mathbf{r})$  becomes small but not precisely zero when  $\Delta U$  becomes appreciable. We can reformulate the linear combination on the general form:

$$\psi(\mathbf{r}) = \sum_R e^{i\mathbf{k}\cdot\mathbf{R}}\phi(\mathbf{r} - \mathbf{R})$$

where  $\phi(\mathbf{r})$  is not exactly an atomic state. If  $\Delta U\phi(\mathbf{r})$ , though nonzero, is exceedingly small, we might expect the function  $\phi(\mathbf{r})$  is really close to the atomic state  $\psi_n(\mathbf{r})$ . Therefore, we seek a  $\phi_n(\mathbf{r})$  that can be expanded in a small number of localized atomic wave function:

$$\phi(\mathbf{r}) = \sum_n b_n \psi_n(\mathbf{r})$$

Starting from the general problem:

$$H\psi(\mathbf{r}) = (H_{at} + \Delta U(\mathbf{r}))\psi(\mathbf{r}) = E(\mathbf{k})\psi(\mathbf{r})$$

knowing that:

$$\langle \psi_m | H_{at} | \psi \rangle = E_m \langle \psi_m | \psi \rangle$$

we find that:

$$(E(\mathbf{k}) - E_m) \cdot \int \psi_m^*(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} = \int \psi_m^*(\mathbf{r})\Delta U(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}$$

equivalent to:

$$(E(\mathbf{k}) - E_m) \cdot \langle \psi_m(\mathbf{r}) | \psi(\mathbf{r}) \rangle = \langle \psi_m(\mathbf{r}) | \Delta U(\mathbf{r}) | \psi(\mathbf{r}) \rangle$$

where  $E_m$  is the energy level of the  $\psi_m$  atomic orbital. Using the definition of  $\phi(\mathbf{r})$  and the last equation we can formulate the general secular equation:

$$\begin{aligned} (E(\mathbf{k}) - E_m)b_m &= -(E(\mathbf{k}) - E_m) \sum_n \left( \sum_{\mathbf{R}} \int \psi_m^*(\mathbf{r})\psi_n(\mathbf{r} - \mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}d\mathbf{r} \right) b_n \\ &+ \sum_n \left( \int \psi_m^*(\mathbf{r})\Delta U\psi(\mathbf{r})d\mathbf{r} \right) b_n + \sum_n \left( \sum_{\mathbf{R}} \int \psi_m^*(\mathbf{r})\Delta U\psi_n(\mathbf{r} - \mathbf{R})e^{i\mathbf{k}\cdot\mathbf{R}}d\mathbf{r} \right) b_n \end{aligned}$$

### 3 Bimolecular Case

Consider now the simple case of two atoms not in a periodic potential. Using LCAO:

$$\psi = c_1\psi_a + c_2\psi_b$$

The secular equation associated to this system is:

$$\begin{aligned} \sum_{m,i,j} (H_{ab}(R_i, R_j) - \epsilon S_{ab}(R_i - R_j))c_m &= 0 \quad b, i, j = 1, 2 (????) \\ H_{ab}(R_i, R_j) &= \int \psi_a^*(r - R_i)H\psi_b(r - R_j)d\mathbf{r} \\ S_{ab}(R_i - R_j) &= \int \psi_a^*(r - R_i)\psi_b(r - R_j)d\mathbf{r} \end{aligned}$$

The last term is called overlap integral. In this case the  $\psi$  are actually the exact atomic wave functions since there is no lattice. The corresponding secular equation is:

$$\begin{pmatrix} H_{12} - \epsilon S_{12} & H_{12} - \epsilon S_{12} \\ H_{21} - \epsilon S_{21} & H_{22} - \epsilon S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

We can now introduce a new set of orthogonalized orbitals using the Lowdin transformation (from atomic orbitals to orthogonal orbitals) simplifying the matrix:

$$\begin{pmatrix} H_{12} - \epsilon & H_{12} \\ H_{12}^* & H_{22} - \epsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

From Slater-Koster tight binding method, within Harrison theory of polar bond, we can write the energy of orbital state as:

$$\epsilon_{ab} = \bar{\epsilon} \pm \sqrt{|H_{12}|^2 + \Delta\epsilon}$$

where:

$$\Delta\epsilon = \frac{H_{11} - H_{22}}{2}$$

$$\bar{\epsilon} = \frac{H_{11} + H_{22}}{2}$$

In this terms,  $H_{12}$  defines the splitting between the two atomic levels while  $\Delta\epsilon$  is related to the polarity of the bond. In the case of real solid, the atoms are not free to move therefore the symmetries of the atomic orbitals must be suitable to create a bonding/antibonding state.

From the first secular equation :

$$(H_{11} - \epsilon)c_1 + H_{12}c_2 = 0$$

using:

$$\epsilon_a = \bar{\epsilon} - \sqrt{|H_{12}|^2 + \Delta\epsilon}$$

we derive:

$$c_1 = \frac{H_{12}}{\Delta\epsilon - \sqrt{|H_{12}|^2 + \Delta\epsilon}} c_2$$

- In the case of homopolar bond, the term  $\Delta\epsilon$  is null and considering normalization conditions on  $c_1$  and  $c_2$ :

$$\begin{aligned} c_1 &= -c_2 \\ |c_1|^2 + |c_2|^2 &= 1 \end{aligned}$$

we can write the coefficients of LCAO:

$$c_1 = -\frac{1}{\sqrt{2}} \quad c_2 = \frac{1}{\sqrt{2}}$$

- In the case  $\Delta\epsilon \neq 0$ , usually, it is defined the degree of polarity:

$$\alpha_p = \frac{\Delta\epsilon}{\sqrt{|H_{12}|^2 + \Delta\epsilon^2}}$$

In the first order approximation ( $\alpha_p \approx 0$ ), we can write the coefficients as:

$$c_1^2 = \frac{1}{2}(1 - \alpha_p) \quad c_2^2 = \frac{1}{2}(1 + \alpha_p)$$

## 4 Jellium Model

The Jellium model is a theoretical model that is used to describe the behavior of a group of electrons in a metal. It assumes that the metal is composed of a uniform positive charge density (often referred to as a "jellium"), which is surrounded by a sea of electrons. The model simplifies the behavior of the electrons by treating them as if they are free to move within the metal and interact only with the positive charge density.

One of the main advantages of the Jellium model is its simplicity, which allows for relatively straightforward calculations of properties such as the electron density, the electronic energy levels, and the conductivity of metals. However, the model has limitations, such as it is not suitable for materials with strong electron-electron interactions or for systems with a low electron density.

### 4.1 Jellium model of surface states

Let's now consider a cleaved bulk. It exposes a geometrical surface at  $z = 0$ . We will consider a gas of free electrons within the surface. In this case we know that, the wave function of free electron is:

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{L\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

where  $L$  is the number of unit cell and  $\Omega$  is the volume of each of these. Note that the translational symmetry is preserved along the  $x - y$  directions, therefore we explicit divide the  $\mathbf{k}$  vector in  $\mathbf{k}_{\parallel}$  and  $\mathbf{k}_{\perp}$ . In our reference we can write the wave function as:

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{L\Omega}} e^{i(k_x x + k_y y)} e^{ik_z z}$$

For our hypothesis, the fermionic gas is confined within the bulk ( $z < 0$ ), therefore the surface must reflect the electrons coming below the surface. Due the linearity of SE, the following wave function is still a solution of the electronic problem:

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{L\Omega}} e^{i(k_x x + k_y y)} (e^{ik_z z} + e^{-ik_z z + \delta})$$

We know that the electron density is linked to the square modulus of wave function:

$$|\psi(\mathbf{r})|^2 = \psi(\mathbf{r})\psi(\mathbf{r})^* = \frac{2}{L\Omega} (1 + \cos(2k_z z - \delta))$$

In the case of free electrons the Fermi surface is represented as a sphere and using cyclic boundary conditions we can write the electron density as:

$$\rho = \int_0^{k_F} |\psi(\mathbf{r})|^2 \pi (k_F^2 - k_z^2) \cdot \frac{L\Omega}{(2\pi)^3} \cdot 2dk_z$$

where we have also consider the spin degeneracy. We have imposed the electron density null at  $z = 0$ , therefore the phase term  $\delta$  must be equal to  $\pi$ :

$$|\psi(\mathbf{r})|^2 = \frac{2}{L\Omega} (1 - \cos(2k_z z))$$

Solving the integral we obtain an electron density of:

$$\rho(z) = \rho_o + 3\rho_o \left( \frac{\cos(2k_z z)}{(2k_z z)^2} - \frac{\sin(2k_z z)}{(2k_z z)^3} \right)$$

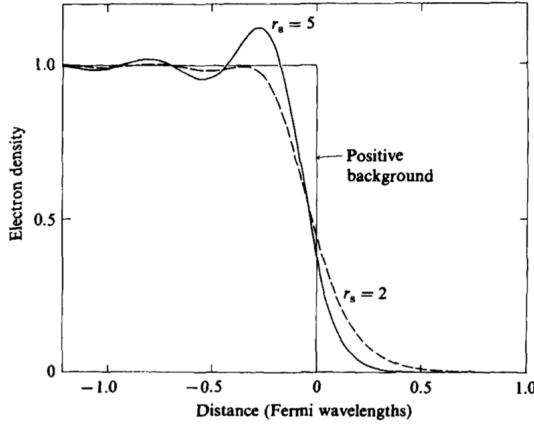


Figure 7: Electron density for  $z_d = 0$

This type of oscillating behaviour for electron density is called Friedel oscillations. The problem is now to define a dividing plane. The distribution of fixed ions is uniform and constant, therefore we must impose charge neutrality:

$$Q^- + Q^+ = 0$$

In our construction:

$$Q^+ = \int_{-\infty}^{z_d} e\rho_o Adz$$

$$Q^- = \int_{-\infty}^0 e\rho(z) Adz$$

where  $z_d$  is the position of dividing plane. The solution of charge neutrality problem give arises:

$$z_d = -\frac{3\pi}{8k_F} < 0$$

This solution is consistent with Gibbs model. The existence of surface excess in terms of electron density defines a surface potential which acts as stopping force for electrons. This uniform distribution of electric dipole creates a potential equal to the case of infinite plane and considering the two sides we have the following potential:

$$\Delta V = \frac{ep}{\epsilon_o A} \approx 0.3eV$$

## 5 Shockley states

In this lecture we will consider the coinage metal  $Ag$  (fcc). Its first Brillouin zone is therefore bcc. Let us consider its (111) surface. For a particular surface, all bulk states with a certain  $k_{||}$  have

to be taken into account. The projection of the bulk modes at a fixed  $k_{\parallel}$  and for all  $k_{\perp}$  yields in the 2D plot a continuous area of possible  $E(k_{\parallel})$  values. In order to generate such plot one has to project the 3D bulk dispersion branches onto the particular 2D surface Brillouin zone; i.e. certain bulk directions and points of high symmetry in the 3D Brillouin zone are projected onto the 2D surface zone:

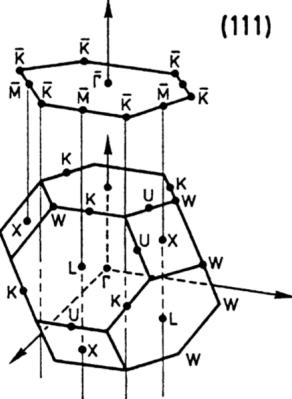


Figure 8: Projection of bulk into the surface, image from [1]

Because of the 2D translational symmetry parallel to the surface, the general form of surface wave function is of Bloch type, i.e. the variation in  $\mathbf{r}_{\parallel}$  enters through the factor  $\exp(i\mathbf{k}_{\parallel} \cdot \mathbf{r}_{\parallel})$  and the energy is increased by  $\hbar^2|\mathbf{k}_{\parallel}|^2/2m$ . The matching condition between the wave function in the bulk and the exponential decay in the vacuum has to be fulfilled for each value  $\mathbf{k}_{\parallel}$ , generally leading to multiple values of energy (as shown in Figure (9)).

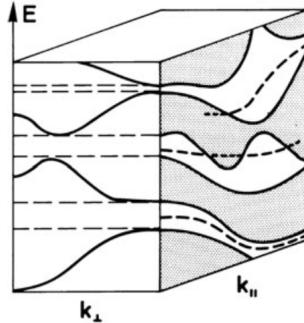


Figure 9: Hypothetical electronic band structure of a crystal. The shaded areas in the  $E(\mathbf{k}_{\parallel})$  plane describe the projected bulk-band structure (along  $\mathbf{k}_{\perp}$ ), image from [1].

True surface state bands are characterized by energy levels that are not degenerate with bulk bands, but they lie in the gaps of the projected bulk-band structures. Surface state bands can also penetrate into a part of surface Brillouin zone, where propagating bulk states exist. They are degenerate with the bulk and can mix with them. These states are called *surface resonances*. Such surface states, developed in the framework of nearly free electron model, are called Shockley states.

## 6 Hybridization

The basic assumption of the discussion of diatomic molecules and crystalline is that the electronic state can be written as linear combination of atomic orbitals. If we take a linear combination between *s* and *p* orbitals we obtain an unsymmetrical probability distribution. In tetrahedral solid (*Si*) we have four *sp* orbitals which form an orthonormal basis and in which the electron density is greatest in direction of the nearest neighboring atom. In general the system *decides* to form hybrid orbitals to increase the overlap of atomic orbitals.

For example in the case of  $sp^2$  hybridization we obtain the following 3 orbitals:

$$\begin{aligned} |sp_1^2\rangle &= \frac{1}{\sqrt{3}}\{|s\rangle + \sqrt{2}|p_x\rangle\} \\ |sp_2^2\rangle &= \frac{1}{\sqrt{3}}\{|s\rangle - \frac{1}{\sqrt{2}}|p_x\rangle + \sqrt{\frac{3}{2}}|p_y\rangle\} \\ |sp_3^2\rangle &= \frac{1}{\sqrt{3}}\{|s\rangle - \frac{1}{\sqrt{2}}|p_x\rangle - \sqrt{\frac{3}{2}}|p_y\rangle\} \end{aligned}$$

The LCAO Hamiltonian matrix, considering only the first neighbors for tetrahedral structure is the type:

$$H_{a,b,i,j} = \left( \begin{array}{c|c} D_A(\epsilon) & (4 \times 4) \\ \hline (4 \times 4) & D_B(\epsilon) \end{array} \right)$$

where we consider the interactions between the  $i$  orbital of atom  $a$  and the  $j$  orbital of the atom  $b$ . The  $D_A$  matrix correspond to the eigenvalue of atomic orbitals:

$$D_A = \begin{bmatrix} \epsilon_s^A & & & \\ & \epsilon_p^A & & \\ & & \epsilon_p^A & \\ & & & \epsilon_p^A \end{bmatrix}$$

The non diagonal block matrix regard the interaction between different atomic orbitals:

$$(4 \times 4) = \begin{bmatrix} E_{ss} & E_{sp} & E_{sp} & E_{sp} \\ & \ddots & & \\ & & E_{pp} & \end{bmatrix}$$

Has been observed that, along specific high symmetry directions it is possible to diagonalize the LCAO Hamiltonian matrix. For example, in the case of *Si* along  $(\bar{\Gamma} - \bar{X})$  direction it is possible to obtain the following solution of secular equation:

$$\epsilon(k) = \frac{1}{4}[\epsilon_s + \epsilon_p \pm E_{ss} \cos(\frac{ka_o}{4})] \pm \{\frac{1}{4}[\epsilon_p - \epsilon_s \pm E_{ss} \cos(\frac{ka_o}{4})]^2 + E_{sp}^2 \sin^2(\frac{ka_o}{4})\}$$

In this picture, the resulting dispersion relation has a direct band gap. This error comes from the hypothesis of considering only the first neighbours.

## 7 DFT

The basic concept of DFT (Density Functional Theory) is that the energy of ground state is function of the electron density. Kohn proved that the ground-state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial coordinates. It set down the groundwork for reducing the many-body problem of  $N$  electrons with  $3N$  spatial coordinates to three spatial coordinates, through the use of functionals of the electron density. The many-body time-independent Schrodinger equation can be written in the following terms:

$$H_{KS}\phi = E\phi$$

where  $H_{KS}$  is the Kohn-Sham Hamiltonian which contains all the interactions:

$$\hat{H}_{KS} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}$$

$$\hat{V} = V_{ion} + V_{Hartree} + V_{ec}$$

The last term represent the exchange correlation. It is generally unknown (except from free electron gas) and different approaches are used to approximate it (Local Density Approximation, Generalized Gradient Approximation, ecc.). Slater proposed an energy related to exchange/correlation term linked to a experimental parameter  $\alpha$ :

$$E_{ec} = -\alpha \frac{9}{8} e^2 \left(\frac{3n}{\pi}\right)^{1/3}$$

He created possible values of  $E_{ec}$  to fit the experimental data. This is called Semi-empirical Method.

## 8 Tamm States

Let us consider a silicon cleaved surface. From a chemical point of view, when we cleaved along a particular axis we cut the bonds in that direction, obtaining a dangling bonds. In this picture the surface species behaves like radical. All this lead to the formation of different electronic states called surface states. Now we can ask ourselves how the system can reduce its energy? We have three possibilities:

- Peierls distortion.
- Charge transfer.
- Passivation.

The **Peierls distortion** consists on a dimerization of the atoms on the surface. As expected, the  $sp^3$  dangling orbitals dehybridize into  $sp_z$ ,  $p_y$  and  $p_x$  orbitals and finally dimerization takes place, as shown in figure.

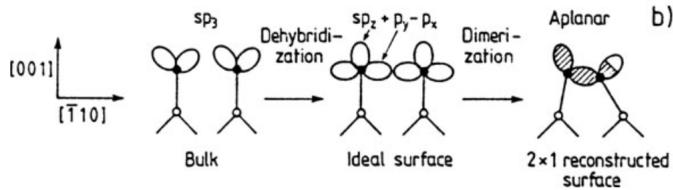


Figure 10: Formation of dimers, image from [1]

The **charge transfer** is linked to the repulsion of the remaining dangling bonds creating asymmetric dimers. The formation of asymmetric dimers can be understood as a Jahn-Teller distortion (removing electronic degeneracy), which leads to a state of lower electronic energy as the degeneracy is lifted by the distortion and the occupied band shifts down below the Fermi-energy.

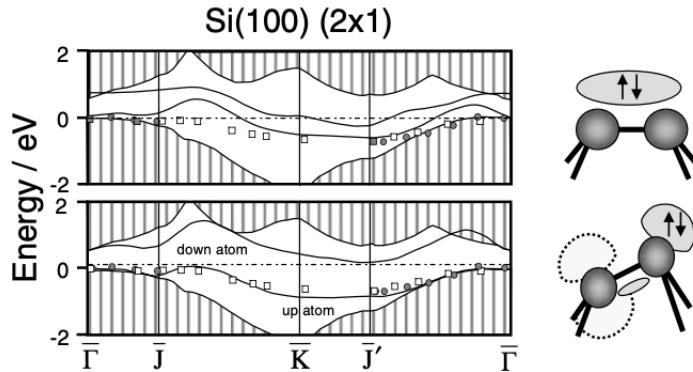


Figure 11: Dimerization and buckling

The figure represent the surface state bands for the symmetric and asymmetric dimer models for Si and Ge, respectively (after Krüger and Pollmann). The dash-dotted lines represent the Fermi-levels. The surface state bands are metallic and insulating for the symmetric and asymmetric dimer respectively, as expected for a Jahn-Teller distortion.

The other mechanism to decrease the surface energy associated to the dangling bonds is **passivation**. Dangling bonds react with new species on surface, which are called adsorbates. The nature of the bonding that is involved in adsorption is addressed by somewhat antiquated terms *physisorption* (physical adsorption) and *chemisorption* (chemical adsorption). In the following, we confine the term physisorption strictly to adsorption mediated by van-der- Waals forces therefore dipole-dipole interaction and dipole-induced dipole interaction.

Strong adsorbate bonding (chemisorption) to a solid substrate must be understood in terms of a chemical reaction, similar to the case of molecular bonding. Covalent adsorption bonds obey essentially the same rules as do covalent bonds between atoms and molecules.

Adsorbed atoms and molecules generally have a significant influence on the electronic structure of a surface: They rearrange the electronic charge within the chemical bond and may also add elementary dipoles if the adsorbed molecule has its own static dipole moment. It is thus necessary to consider the work function of a solid surface in more detail, in particular in the presence of an adsorbed species. As already discussed in the jellium model, the excess of surface electron density defined a surface potential:

$$\Delta V = \frac{ep}{\epsilon_o A}$$

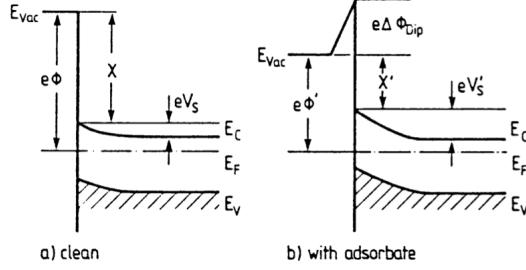


Figure 12: Chemisorption and work function, image from [1]

In the figure (b) chemisorption bonding of an adsorbate generally changes the band bending into  $eV'_s$ ; charge transfer within the chemisorption bond induces dipoles within the surface and thus changes the work function and the electron affinity into  $e\phi'$  and  $\chi'$ , respectively (dipole contribution  $e\Delta V$ , in the figure  $e\Delta\phi_{Dip}$ ).

The charge transfer depends on the coverage of chemiadsorbate. A typical case is  $Cs$  on top of  $Ag(111)$ . As shown in figure there is a minimum of work function for 0.4 normalized coverage.

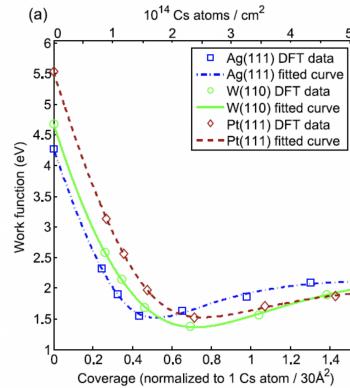


Figure 13: Coverage and work function, Chou, Sharon. (2014). Discovering low work function materials for thermionic energy conversion.

## 9 The chemical bond of adsobate on metals

We now try to discuss charge transfer related to covalent bonds of chemical adsorbate based on Blyholder model. Let us take in consideration passivation with *CO* of metal surface (ex. *Pt(111)*). For the *CO* the **LUMO** and **HOMO** are respectively the  $2\pi^*$  and the  $5\sigma$ . The energies of both orbitals with reference to the vacuum level lie near the Fermi-level of transition metals. The  $5\sigma$ -orbital forms bonding and antibonding combinations with the unoccupied metal states and thereby establishes a chemical bond to which the CO-molecule contributes two electrons. Thereby charge is donated to the surface.

The  $2\pi^*$ -orbitals form bonding and antibonding combinations with the occupied metal states. Electrons from the metal are back donated into the molecule. Since the  $2\pi^*$ -orbital is an antibonding orbital for the CO-molecule this back donation weakens the internal chemical bond of the CO molecule.

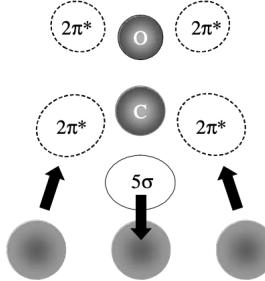


Figure 14: Charge transfer (the arrows) for CO-molecule on top on transition metal.

The different orientations of  $2\pi^*$  and  $5\sigma$  suggest different preferred sites for the two molecular orbitals. For the  $2\pi^*$ , the bridge site between two metal atoms provides the best overlap while for the  $5\sigma$  the best overlap is for a-top side. The two effects compensate each other and therefore the CO-chemisorption is not site sensitive.

We can now generalize this construction, based on charge transfer from HOMO and LUMO to metal surface states. Linear combination of metal surface state and HOMO/LUMO forms other bonding and anti-bonding levels. Based on the position of surface state and HOMO/LUMO (for the molecule) we can have 4 types of charge transfer.

- Case 1: the surface state is above the Fermi energy and the HOMO is below it. In this case, the molecule gives electron to the system behaving as donor.
- Case 2: the surface state is below the Fermi energy while the LUMO is above it. In this case the surface state gives electrons to the system (anti-donor behaviour). This is analogous to the  $2\pi^*$  charge transfer in CO-chemisorption.
- Case 3: the surface state and HOMO are below Fermi energy. The interaction between this two states produces a bonding state and anti-bonding state each one full-filled. Now the filled anti-bonding is above the Fermi energy therefore is convenient for the system to transfer charge from this state to the Fermi sea. Note that the bonding electrons must come from the molecule.
- Case 4: even the surface state and the molecular state (LUMO) are above Fermi energy. Therefore the electron from the Fermi surface on the surface are transferred to the bonding level. In this case charge is transferred from the surface.

## 10 The *Si(111)* case

One of the most studied semiconductor surface is *Si(111) cleaved surface*. We have already discussed the presence of reconstruction, which depends on environmental parameters like pressure and temperature.

If the crystal is cleaved at room temperature, a  $(2 \times 1)$  reconstruction is found in LEED. If cleaved at very low temperature ( $T < 20K$ ) a  $(1 \times 1)$  LEED pattern appears. After annealing to temperatures higher than about  $400^\circ\text{C}$  a  $(7 \times 7)$  super-structure occurs indicating an extremely

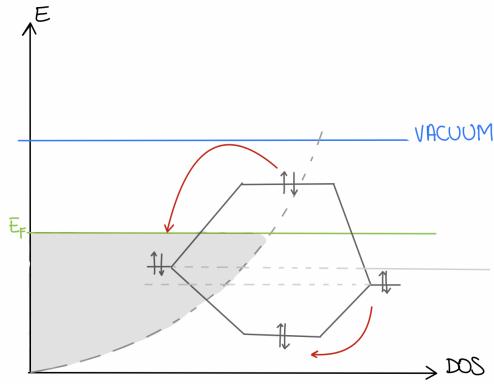


Figure 15: On the left surface state. On the right molecular state.

long-range periodicity. The  $(7 \times 7)$  structure is definitely the most stable configuration; the  $(1 \times 1)$  and the  $(2 \times 1)$  structures are frozen-in metastable configurations.

The Si $(2 \times 1)$  surface has attracted much attention in recent years. Independent of the reconstruction model considered, there is an interesting argument that the  $(2 \times 1)$  reconstruction splits the half-filled dangling-bond surface-state band within the bulk gap into two parts. The 2D Brillouin zone shrinks by a factor of two in one direction for the  $(2 \times 1)$  structure i.e., for symmetry reasons, one half of the dangling-bond band can be folded back into the new  $(2 \times 1)$  Brillouin zone thus opening up a gap at the  $(2 \times 1)$  zone boundary.

Since the original  $(1 \times 1)$  band was half filled, this splitting into an empty upper branch and a full lower branch leads to a total energy decrease and thus to a stabilization of the  $(2 \times 1)$  structure.

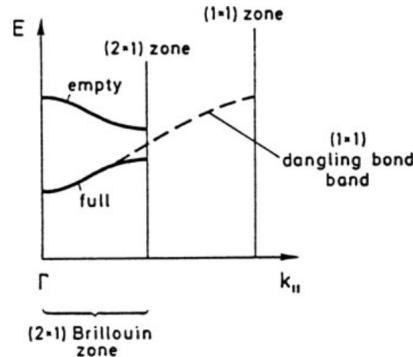


Figure 16: Reduction of Brillouin zone, image from [1].

For a long time the so-called buckling model had been assumed to explain the double periodicity on the cleaved Si(111)-(2  $\times$  1) surface with little dispersion along the  $\Gamma J$  symmetry line of the  $(2 \times 1)$  surface Brillouin zone. This is in contradiction to the experimental findings from ARUPS (see figure below) . A number of different groups have experimentally observed strong dispersion along  $\Gamma J$  (direction of Pandey-chain).

This finding, and all other experimental data so far can be explained in terms of the so-called  $\pi$ -bonded chain model of Pandey. Complete Si-Si bond breaking is required in the second atomic layer to induce this reconstruction. But the resulting zig-zag pattern allows the dangling  $p_z$  bonds of the topmost layer to form one-dimensional  $\pi$ -bonds just like in a one-dimensional organic system.

Tight Binding approach to isolated one-dimensional Pandey chain leads to:

$$\epsilon_{\pm} = \frac{1}{2}(\epsilon_1 + \epsilon_2) \pm \sqrt{\frac{1}{4}(\epsilon_1 - \epsilon_2)^2 + (H_{12}(d_1) + H_{12}(d_2))^2 \cos^2\left(\frac{ka_o}{2\sqrt{2}}\right)}$$

which suggest a metallic behaviour of the system along the chains. To minimize the energy the system decides to buckle the  $\pi$ -chain (see red and green atoms in Figure (18)).

More advanced calculations based on GW band-structure theory show different energy levels for positive and negative buckling. According to the band structures calculated, the band gap is smaller

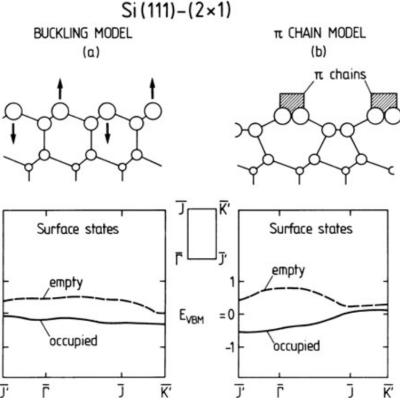


Figure 17: Discrepancy between simple buckling model and Pandey chain model, image from [1].

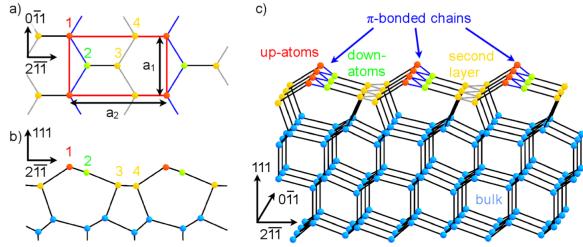


Figure 18: Pandey chain model of Si reconstruction

for negative buckling ( $E_{Gn} = 0.58\text{eV}$ ) than for positive buckling ( $E_{Gp} = 0.75\text{eV}$ ), and the surface bands for negative buckling lie within the surface band gap of positive buckling.

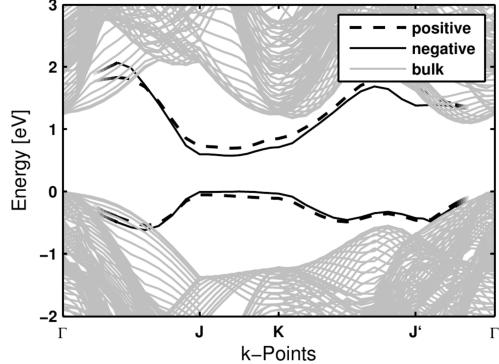


Figure 19: Calculated electronic surface dispersion resulting from the GW band-structure theory.

## 11 Band bending

If one puts a positive point charge into a locally neutral electron plasma (electrons on the background of fixed positive cores), the electrons in the neighborhood will rearrange to compensate that additional charge; they will screen it, such that far away from the charge the electric field vanishes.

A semiconductor surface which possesses electronic surface states usually represents a perturbation to the local charge balance. Depending on the type of surface states (donors or acceptors) and on the position of the Fermi level at the surface, the surface states may carry charge, which is screened by an opposite charge inside the semiconductor material.

The position of the Fermi level at the surface is determined simply by the condition of charge neutrality, namely that the charge of the surface states  $Q_{ss}$  is compensated by an opposite charge inside the semiconductor. This latter charge screens the surface-state charge, and is called the space

charge  $Q_{sc}$ . The condition that must be satisfied is:

$$Q_{sc} = -Q_{ss}$$

In the following figure is represented the interface of an acceptor-like surface and a n-doped semiconductor. The negative charge in the surface is compensated by ionization of donor atom inside the bulk by means of band bending. This extension of ionized atoms is called space charge layer.

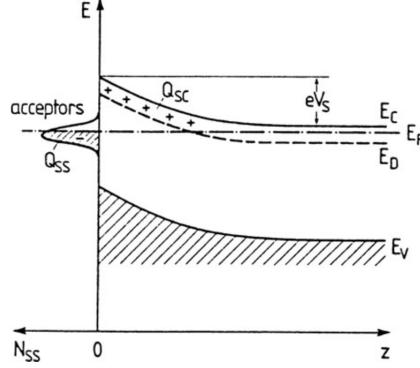


Figure 20: Acceptor-like surface and n-doped semiconductor, image from [1].

The fundamental equation which governs band bending  $V(z)$  and the form of the space-charge layers, in general, is Poisson's equation:

$$\frac{d^2V}{dz^2} = -\frac{\rho(z)}{\epsilon_r \epsilon_o}$$

This equation directly relates the band curvature to the space-charge density  $\rho(z)$ . Usually it is sufficient to consider the dependence on the single coordinate  $z$  directed perpendicular to the surface (located at  $z = 0$ ). Let us approximate the space charge density with a step like function. The Poisson's equation becomes:

$$\begin{aligned} \frac{d^2V}{dz^2} &= -\frac{eN_D}{\epsilon_r \epsilon_o} \\ E(z) &= \frac{eN_D}{\epsilon_r \epsilon_o}(z - d) \end{aligned}$$

and the further integration, at the surface:

$$V_s = -\frac{eN_D}{\epsilon_r \epsilon_o}d^2 \quad V_s \text{ is called Schottky potential.}$$

Assuming  $N_{ss}$  to be  $10^{12} cm^{-2}$  requires a space charge density  $Q_{sc} = eN_D d$ , of equal magnitude and a thickness  $d$  of the depletion space charge layer of about 1000 Å results!

Allen and Gobeli shown the existence of a sort of pinning of Fermi energy from the presence of surface states. Generally, without considering the surface state, the variation of work function with the doping level of the semiconductor should be linearly (in logarithmic scale). The figure shows (continuous line) a plateau of values for which the work function doesn't change.

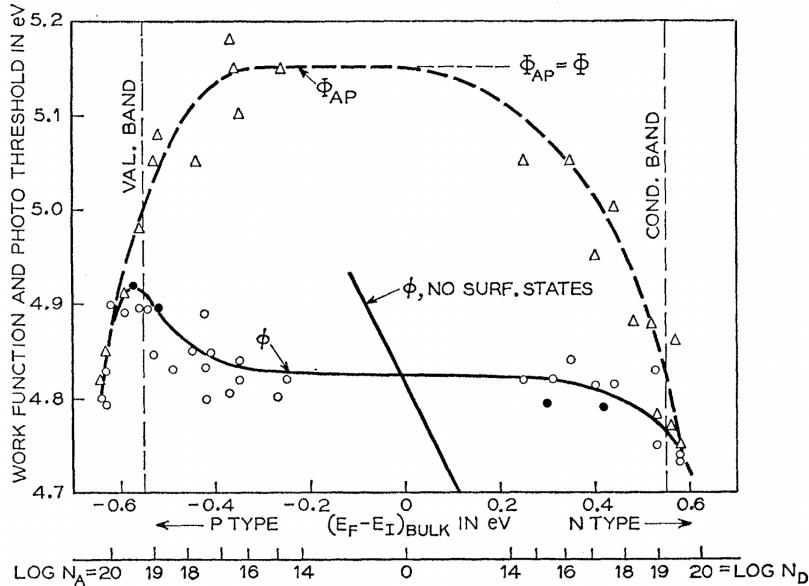


Figure 21: Allen and Gobeli experiment, image from [1].

## 12 Interfaces

### 12.1 Metal-metal junction

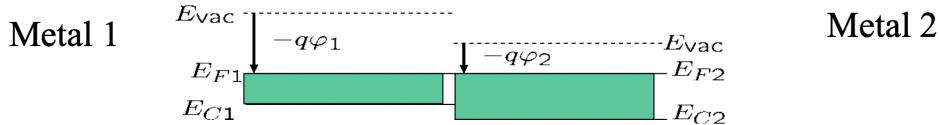


Figure 22: Junction of different metals

The different values of work function for this metals creates a dipole characterized by a contact potential  $\Delta V_c = e(\gamma_1 - \gamma_2)$ . This is the basis of Volta effect.

Now the question is: how can I measure the contact potential? We link the two metals by an amperometer and place them at a certain distance. This system behaves like a capacitor:

$$Q(t) = C(t)\Delta V_c$$

$$\frac{dQ}{dt} = \frac{dC}{dt}\Delta V_c = I$$

Varying the distance between the two metal also the capacitance varies and therefore a current is produced. Usually the tip metal is a known metal used as a probe to investigate the other metal. Placing a voltage generator in series with the amperometer we have a relative measurement of the work function of the metal:

$$I = \frac{dC}{dt}(\Delta V_c + \Delta V_{bias}) = 0$$

$$V_{bias} = -(\phi_M - \phi_{probe})$$

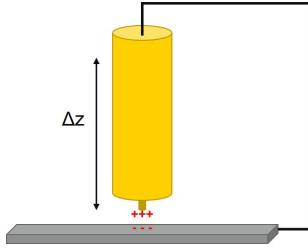


Figure 23: Kelvin probe microscopy

## 12.2 Metal-semiconductor junction

We now consider an ideal metal-semiconductor junction. As a first approach one might apply the same arguments based on the work function to give some initial insight into the problem. In thermal equilibrium the Fermi levels in the two material must be the same. Depending on the work function  $e\phi_M$  of the metal and the electron affinity  $\chi_{sc}$  different situations may arise. When the two sample are brought to contact the Fermi levels invariability causes charge to flow from one side to the other. Then a dipole layer is built up at the interface. Into the metal this dipole is screened within few Angstroms while in the semiconductor the lower density of carriers lead to a less efficient screening. Therefore the space charge layers extends over several hundreds of Angstroms as in the case of surface states on a clean surface . Let us take the diagram (a) in the figure (18). The maximum band bending  $eV_B$  at the interface is related to the potential barrier  $e\phi_{SB}$  (called also Schottky barrier) which has to be overcome when an electron is excited from the metal into the conduction band of the semiconductor. According to this simple picture a knowledge of metal work function  $e\phi_M$  and of the electron affinity  $\chi_{sc}$  of the semiconductor would allowed one to predict the Schottky barrier. This approach was first applied to understand the rectifying action of metal-semiconductor junctions.

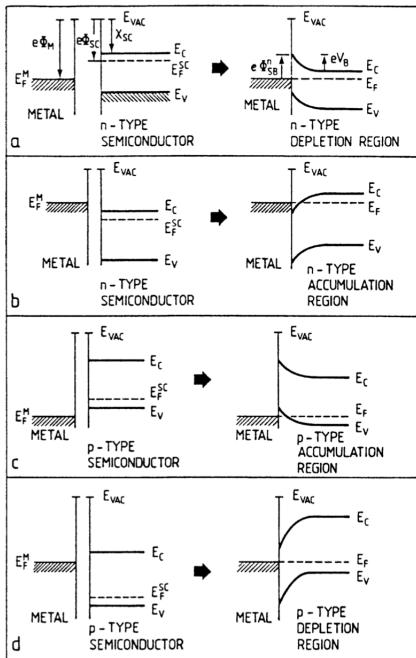


Figure 24: Schematic diagrams of band bending before and after metal-semiconductor contact: (a) High work-function metal and n-type semiconductor, (b) low-work-function metal and n-type semiconductor, (c) high-work-function metal and p-type semiconductor, and (d) low-work-function metal and p-type semiconductor, image from [1].

Let us take metal covered n-type Si(111)-(2x1) cleaved surface. According to Schottky model one would expect a much greater variation of the barrier height with work function than is experimentally observed (25). Apart that the work function concept for a clean metal surface cannot be extended to the interfaces, when the metal atoms come into close contact with the semiconductor surface, they will form chemical bonds whose strength will depend on the nature of the partners. The distribution of clean surface state of the semiconductor may change. In addition charge may flow from one side to the other due to the formation of the bonds as we have seen in the Blyholder model. This can be modeled as a dipole of atomic scale. In this case one can expect the formation of new electronic interface states. To explain the experimental data of Schottky barrier height in function of metal work function, Bardeen assumed that the surface states persist under the metal layer and that they

pin the Fermi level. The work function of the deposited metal would thus have no effect on the position of the Fermi level at the interface. For metal coverages in the monolayer range ( $\theta = 1$ ) which are unable to screen interface charge, surface-state densities as low as  $10^{-12} \text{ cm}^{-2}$  could pin the Fermi level at a fixed position.

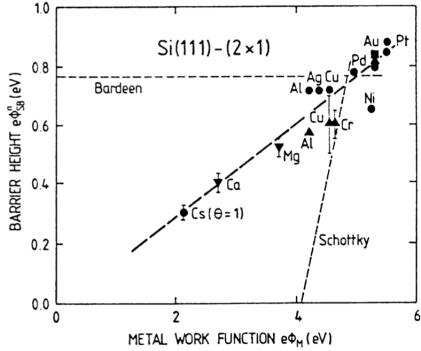


Figure 25: Barrier height of Si-Schottky barrier versus different metal work function, image from [1]

## 13 Metal-Induced Gap States (MIGS)

Numerous experiments on a wide variety of metal-semiconductor systems prepared under UHV conditions indicate that the deposition of metal films produces interface states which determine the position of the Fermi level at the interface. Well-known examples are metal overayers on cleaved GaAs(110) surfaces. A clean, well-cleaved GaAs(110) surface usually has flat bands, i.e. the forbidden band is free of surface states.

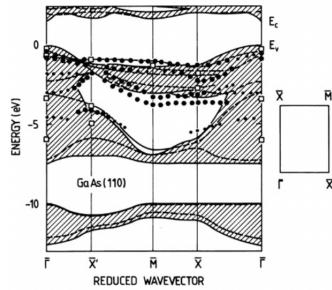


Figure 26: Measured and calculated dispersion curves of surface states (solid lines) and surface resonances (dashed lines) on cleaved GaAs(110) surfaces along the symmetry lines of the surface Brillouin zone (right-hand side). The shaded areas represent the projected bulk band structure. It is well known that on a perfectly cleaved surface with mirror-like finish, the Fermi level is not pinned; the bulk-band gap should essentially be free of surface states, image from [1].

Deposition of metal atoms causes band bending in both p- and n-type materials. For n-type material an electron depletion layer is formed with the Fermi level  $E_F$  pinned at about 0.8 eV above the valence-band maximum  $E_V$ . This pinning of  $E_F$  is caused by interface (or surface) states with a minimum density of about  $10^{-12} \text{ cm}^{-2}$ . What is the nature of these interface states? Heine put forward the idea that metal (Bloch) wave functions tail into the semiconductor in the energy range in which the conduction band of the metal overlaps the forbidden band of the semiconductor. The breakdown of periodicity at the interface introduces exponentially decaying interface states with imaginary wave vectors  $\kappa = -iq$ . Dispersion curve  $E(q)$  “fills” the energy gap of the semiconductor symmetrically with respect to the band edges  $E_C$  and  $E_V$ . These gap states have a density of states with singularities near  $E_C$  and  $E_V$ . The existence of such states and their properties depend on the boundary condition at the interface.

## 14 Optical Surface Techniques

Now the problem is: how to investigate the existence of MIGS? **Light!**

The problem associated to light is its penetration. Usually the probing depth of light in bulk is in the same order of wavelength of light ( $\approx 500 \text{ nm}$ ). In principle, the surface sensitivity is always achieved by measuring difference signals which enhance the surface contribution with respect to that of the bulk or substrate. Since semiconductors are transparent for light of photon energy below the bandgap energy ( $\hbar\omega < E_g$ ), surface excitations such as electronic surface state transitions and vibrations of adsorbed molecules, can be detected by internal reflection in which the light beam probes the optically absorbing surface region from inside the crystal. Surface states are enhance

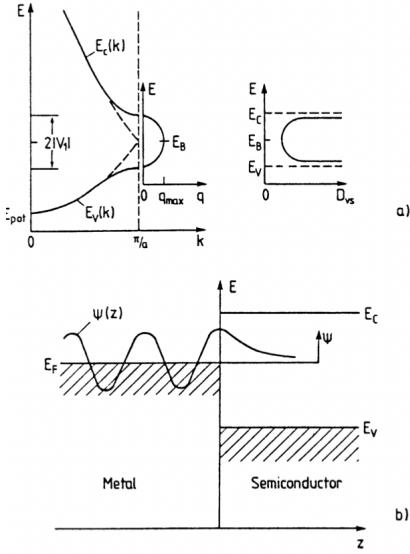


Figure 27: Origin of Metal-Induced Gap States (MIGS) at a metal–semiconductor interface.(a) Dispersion of a one-dimensional chain of atoms (model of semiconductor); the real band structure with  $E_C(k)$  and  $E_V(k)$  as conduction and valence bands, respectively, is obtained for an infinite chain. For a finite chain, exponentially decaying interface states with imaginary wave vectors  $\kappa = -iq$  fill the gap of the semiconductor between  $E_C$  and  $E_V$ , and in the simplest case are symmetric about the so-called branching point energy  $E_B$ . The density of states  $D_{VS}$  of these states has singularities near  $E_C$  and  $E_V$ . (b) Qualitative representation of a metal Bloch state (near  $E_F$ ), decaying into the semiconductor. The tail of the wave function arises because  $\psi(z)$  cannot change abruptly to zero in the semiconductor, where no electronic states exist in the forbidden band,image from [1].

crystals whose shape allow multiple reflection. This experiment based on differential signal between clean Ge(111) surface and oxidize Ge(111) surface was performed for the first time in 1965 by Chiarotti et al. The differential signal  $\Delta R/R$  is measured for different incoming photon wavelength:

$$\frac{\Delta R}{R} = \frac{R_{clean} - R_{ox}}{R_{ox}}$$

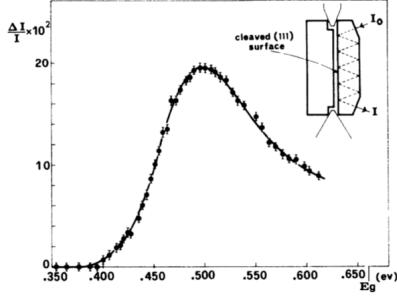


Figure 28: Variation of the intensity of light totally reflected at a cleaved surface of intrinsic Ge at room temperature after the oxidation of the surface, as a function of the energy of the photons.

The relative attenuation of the internally reflected light intensity was recorded for the clean cleaved Ge surface and for the same surface after oxygen adsorption. In the latter case the transmitted intensity was higher due to the removal of the surface state transitions. The corresponding spectral dependence of the surface state absorption indicates surface state transitions near 0.5 eV photon energy.

The theoretical explanation of Chiarotti's peak is based on the 3-layers model. Since it is impossible to take in account all the layers (the usual problem of define the surface, i.e different properties for different layer) we approximate our model on 3 layers: vacuum, surface and bulk. We will consider the dielectric function be homogeneous for each layer and the surface length  $d$  such that  $d \ll \lambda$ . In this approximation we can use the concept of Fresnel interface.

Let us consider a monochromatic light:

$$\mathbf{E} = E_0 e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})}$$

In the Fresnel framework we can derive the reflectivity Fresnel coefficients:

$$r_{jk\parallel} = \frac{\mu_k \xi_j - \mu_j \xi_k}{\mu_k \xi_j + \mu_j \xi_k}$$

$$r_{jk\perp} = \frac{\epsilon_k \xi_j - \epsilon_j \xi_k}{\epsilon_k \xi_j + \epsilon_j \xi_k}$$

where  $j, k = 1, 2, 3$  indicates the layer. Rewriting the refractive index and the dielectric constant in terms of real and imaginary part, we can write the following identity:

$$\hat{\epsilon}_j = \epsilon_j' + i\epsilon_j'' = (1 + 4\pi\alpha_j) - i\left(\frac{4\pi\sigma_j}{\omega}\right)$$

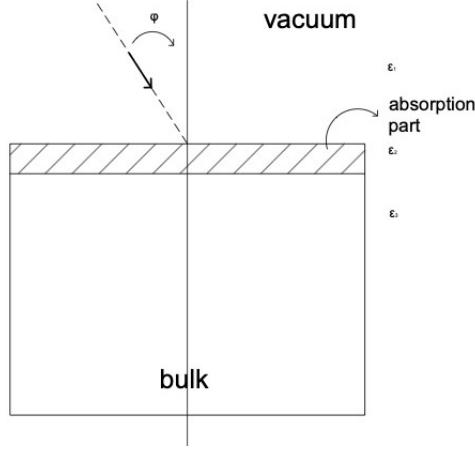


Figure 29: The three layers model

where  $\alpha_j$  is the polarizability and  $\sigma_j$  is the conductivity. For the overall system (three layers) in the approximation of small thickness in comparison with the wavelength, we have:

$$r_{123} = \frac{r_{12} + r_{23}(1 - 2i\beta)}{1 + r_{12}r_{23}(1 - 2i\beta)}$$

$$\beta = (2\pi n_2 \cos\phi_2) \frac{d}{\lambda}$$

Can we interpret the SDR experiment with the three layer model?

We know the reflectivity is the square modulus of the Fresnel coefficient:

$$R(d) = |r_{123}|^2$$

$$R(0) = |r_{13}|^2$$

Therefore the differential signal can be seen as:

$$\frac{\Delta R}{R} = \frac{R(d) - R(0)}{R(0)} = \frac{R(d)}{R(0)} - 1 = \left| \frac{r_{123}}{r_{13}} \right|^2 - 1$$

$$\frac{\Delta R}{R} = 8\pi n_1 \frac{d}{\lambda} \operatorname{Im}\left(\frac{\hat{\epsilon}_2 - \epsilon_3}{\epsilon_1 - \hat{\epsilon}_2}\right)$$

We can conclude that if we consider a very thin absorbing layer and perform DFT calculation to obtain the dielectric constant of the surface, we obtain the same peak in the differential signal.

Does the optical transition gives you the actual energy gap from surface states?

In principle no! Once we excite an electron in conduction band an exciton is created (quasi-particle). In material with many electron this exciton is screened so the optical transition is in the range of the energy gap. In semiconductor exciton binding energy is in the order of 0.3eV. In *Si*(111) – (2x1) the correlated electron-hole must be along the same Pandey chain. This correlation has been seen within 120nm! Suppose now we want to passivate oxygen on top of silicon. The oxygen (very reactive element) will destroy the  $\pi$  chains and therefore also the Frenkel exciton. There will be a confinement of 1D chain.

## 15 Reflective anisotropy spectroscopy

Another optical technique to investigate surface state is reflective anisotropy spectroscopy (RAS). It is a non destructive optical probe of surfaces that is capable of operation within a wide range of environments. RAS measures the difference in reflectance ( $\Delta r$ ) of normal incidence plane-polarized light between two orthogonal directions in the surface plane (x, y) normalized to the mean reflectance ( $r$ ):

$$\Delta r = \frac{r_x - r_y}{\frac{r_x + r_y}{2}}$$

In general, as seen for SDR, light is not sensitive to surface since it can penetrate several layer into the bulk. Here the point is that cubic lattice system response to RAS is isotropic and therefore any response to RAS measures come from possible anisotropy of the surface.

An example of the application of RAS is the  $Si(100) - (2x1)$  vicinal surfaces. We know that the  $(2x1)$  reconstruction implies a dimerization with the buckling of the dimers. Therefore two types of vicinal surface can be produced based on the exfoliation of the substrate: with dimers perpendicular to the step or dimers parallel to the step. Based on the RA spectrum we can investigate the orientation of the dimers on the system.

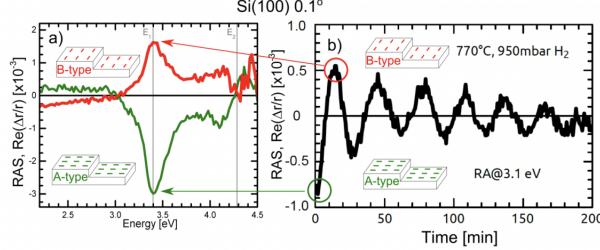


Figure 30:  $Si(100) 0.1^\circ$

Note that the RAS signal meaning is not straightforward. The RAS measures the difference in reflection between the anisotropic complex Fresnel amplitude reflection coefficient along particular crystallographic axis and it contains a real and imaginary part. Therefore RAS is clearly linked to the dielectric function of the surface.

Talking about vicinal surface, we can introduce surface effect like the Ehrlich-Schwoebel barrier. These barriers arise from the interaction between atoms or molecules diffusing across a step edge on a crystal surface. When a crystal surface contains a step, which is a discontinuity in the atomic arrangement, atoms or molecules can move along the step edge. However, the process of crossing the step edge is not always straightforward due to the Schwoebel barrier. This barrier arises because the coordination environment of atoms at the upper terrace of the step is different from that at the lower terrace.

We can have several behaviour of the barrier. For example, we can wave a sticky barrier or a reflective barrier. The presence of Schwoebel barriers has significant implications for the growth and patterning of thin films, as they can influence the step-edge morphology and surface roughness

### 15.1 Cs coverage of GaAs(110)

It is well known that the cleaved GaAs(110) surface does not present any surface state (or better, surface states are degenerate with the bulk projected states). In the range below 0.1 coverage Cs forms 1D structure (self-assembled nanowires). We can investigate the nature of these nanowires using Reflective Anisotropy Spectroscopy since the bulk zinc-blende  $III - V$  semiconductors are optical isotropic. Using the three layer model, the RAS signal can be written as:

$$Re\left(\frac{\Delta r}{r_m}\right) = \frac{4\pi d}{\lambda} \cdot Im\left(\frac{\Delta\epsilon}{\epsilon_b - 1}\right)$$

Along the  $[1\bar{1}0]$  direction STM reveals zig-zag 1D structures. This phenomena has very interesting applications since we have auto-assembling structures just after sublimation of Cs on mesoscopic scale. In principle we can expect a metallic behaviour of this nanowire. The optical properties of simple metal have been studied by Drude. I expect to obtain the Drude tail (in IR region) for the RAS signal since it is related to the imaginary part of the dielectric tensor.

In Figure (31) the RAS signal has been plotted from  $\theta = 0$  (no Cs sublimation) to  $\theta = 0.1$ . The expected enhancement of reflectivity in the IR region has not been observed. Moreover structures related to transition between clean surface states (surface resonances) are quenched. This Cs state transition from metal to insulator is related to the weak overlap of Cs orbitals. In metallic Cs the lattice constant is in the order of  $a_{Cs} = 6.1 \text{ \AA}$  while in Cs/GaAs the lattice constant is  $a_{Cs} = 6.9 \text{ \AA}$ .

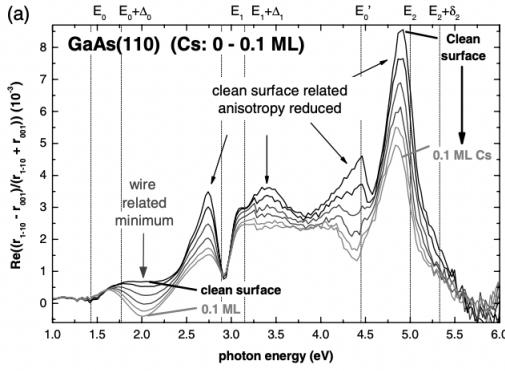


Figure 31: Shows the spectra from the clean surface to 0.1 ML coverage, K Fleischer et al 2004 J. Phys.: Condens. Matter 16 S4353.

## 15.2 Stable alignment of tautomers at room temperature for porphyrin 2D layer

A major challenge in molecular electronics is to develop logic devices based on truly intra-molecular mechanism. In porphyrins the switching mechanism is mediated by the bistability of position of the two hydrogen atoms which can occupy different, but energetically equivalent positions in the inner cavity of the porphyrin. Up to now, such a reaction has only been exploited at low temperatures and induced or detected through atomic scale manipulation. Additionally, unpredictable orientation of molecules preclude any electronic functions.

An evidence based on the exploitation of surface effect of HOPG shows a frozen tautomerization of  $H_2TPP$  molecule even at room temperature with the H position settled a priori. The preferential alignment of tautomers, which can be chosen a priori by a specific exfoliation procedure of the HOPG, makes the overall optical properties of the porphyrin layer anisotropic.

Exposing  $H_2TPP$  to  $HCl$  vapor, we add more H-atoms to the porphyrin resulting in the formation of  $H_4TPP$ . To return to the previous state we can simply use an heat pulse. The reading of the state-flip can be done using polarized light since  $H_4TPP$  is optical isotropic.

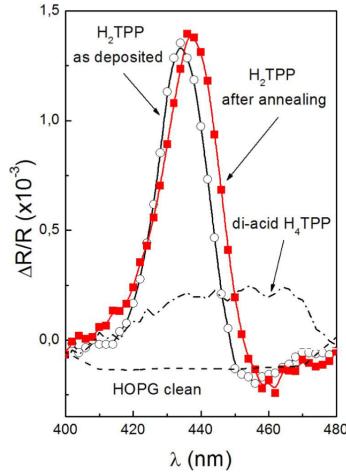


Figure 32: RA spectra of  $H_2TPP$  based switch.

Note that, HOPG (Highly Oriented Pyrolytic Graphite) is an ideal substrate since it is conductive and optical isotropic.

Now the problem is to realize the specific geometry of the system. For example I want to deposit porphyrin molecules in a particular pattern on the surface. The problem which can arise from the simplistic surface model is not to consider surface ligand effects. In general we can say that the surface atoms can change the properties of the deposited molecule and viceversa. How can I obtain an ideal surface?

- Quench the surface ligand effects.

- Exploit surface ligand effects to drive a specific coordination of the molecules.

## 16 Surface Defects

The thermodynamic energy of formation of **vacancies**  $\Omega_f$  is related to the  $\Delta E$  of the two surfaces, the chemical potential and the variation of electron properties. For a two component system A and B, with a vacancy of atom B, we can write:

$$\Omega_f = E(N_A, N_{B-1}, q) - E(N_A, N_B) + \mu_B + q(E_f + E_{VBM})$$

We can expect a relaxation of the system near the vacancy. The creation of vacancy in general should add some state in the forbidden region, and can be probed using optical spectroscopy. Let us take the Si(111)-(2x1) surface, with a vacancy. The defect introduce energy levels in the forbidden

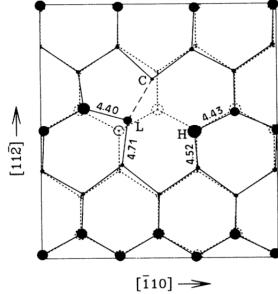


Figure 33: A top view of the first two planes. The  $\pi$  chains are along the [-110].

region. The defect states are called  $v_1$ ,  $c_1$  and  $c_2$ . Performing a STM experiment we can retrieve the LDOS. In the following image we have the LDOS for no-defects (b) and defects(c). We can see that there are an enhancement of LDOS for the energy levels of the vacancy. Let us consider another

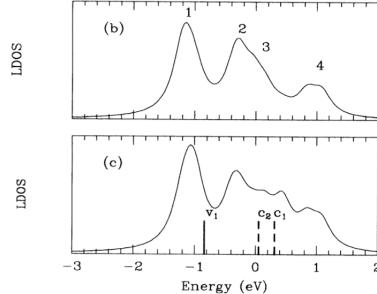


Figure 34: LDOS for no-defects (b) and defects after relaxation (c).

type of 0D defects, the **impurities**. One atom of the lattice is substituted with another atom (F). As done before, the formation energy with the removal of the B atom and adding the F atom is:

$$\Omega_f = E(N_A, N_{B-1}, F, q) - E(N_A, N_B) + \mu_B - \mu_F + q(E_{VBM} - E)$$

where the last term is related to electron reservoir of the system. The **antisites** are defects in which one atom A is substituted by an atom B. The formation energy is:

$$\Omega_f = E(N_{A-1}, N_B, q) - E(N_A, N_B) + \mu_B - \mu_A + q(E_F + E_{VBM})$$

Usually it is written as:

$$\Omega_f = E(D, f) - E(N_A, N_B) + \sum n_A \mu_A \pm \frac{1}{2} \Delta \mu + V_{\text{correction}}$$

Therefore, while for impurities and vacancies the charge of single element is counted in a linear way, for antisites the situation is more complicated. We have to fit the model with the experimental data.

## 17 Electron-Phonon interaction in optical absorption for Si(111)-(2x1)

We have seen that the Si(111) cleaved surface reconstructs on a (2x1) lattice with the formation of 1D chains (Pandey chains). The Surface Differential Reflectivity (SDR), i.e. the ratio between the difference in reflectivity of clean silicon surface and oxidized one and the reflectivity of the oxidized one, is proportional to the imaginary part of electron susceptibility (and therefore the dielectric function) and it is linked to the absorption coefficient of the material.

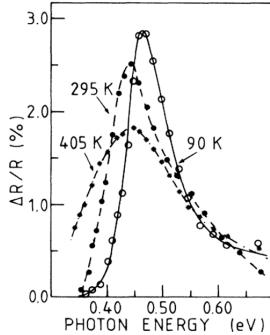


Figure 35: SDR spectra of Si(111)-(2x1)

The maximum of absorption coefficient displays a red shift with the temperature while its full width half maximum increases considerably. Moreover the shape of the curve is asymmetric, being wider in high-energy side. The large broadening of the spectra suggest an important electron-phonon interaction for the 2x1 surface. The full width at half maximum in function of the square root of the temperature is almost linear as displays in the following image.

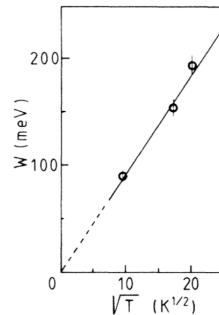


Figure 36: FWHM dependence on  $\sqrt{T}$

## 18 Reactions on surfaces

In the last years, surface are used as catalyst in many industrial reactions. As already known, the reaction rate follows an Arrhenius law:

$$k_r = \nu e^{-E_r/RT}$$

where  $E_r$  is the barrier energy for the reaction. Using surfaces it is possible to change the barrier energy  $E_r$  and the formation enthalpy  $\Delta H_f$ . Therefore it is possible that we have an higher reaction rate but a smaller amount of products. The relation between the energy barrier and the variation of enthalpy has been formulated in the BEP hypothesis (1938). The variation in the energy barrier is proportional to the variation of formation enthalpy. This hypothesis has been demonstrated in 2008 for methane/Pt(001).

### 18.1 Ammonia synthesis

As seen, we can exploit the catalytic effect of surfaces to improve the rate of synthesis of NH<sub>3</sub>:



Using different surface we can vary the formation rate of  $\text{NH}_2$ , an reaction intermediate which limits the overall kinetics.

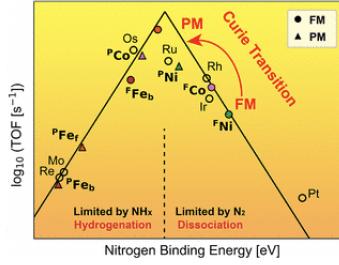


Figure 37: The volcano plot

The left side zone is limited by the desorption of  $\text{NH}_3$  from the surface, i.e. we can produce ammonia but it is impossible to stabilize it. On the other side of the plot, the rate is limited by the molecular nitrogen dissociation on the surface.

We can distinguish two chemical mechanism on surface for bi-molecular reaction:

- **Rideal mechanism:** only one specie is thermalized (dissociated) on the surface while the other one remain in gas phase and reacts whit the adsorbate.
- **Langmuir mechanism:** both species are dissociated on the surface and chemical reaction happens for diffusion on it.

## References

- [1] H. Lüth. *Solid Surfaces, Interfaces and Thin Films*. Graduate Texts in Physics. Springer International Publishing, 2014.