Appendix C

Theory of Scanning Tunneling Microscopy (STM)

Scanning tunneling microscopy (STM), which was introduced by Binnig and Rohrer at 1982, is an experimental technique for studying surfaces. In this technique the electronic structure of surfaces is probed, by utilizing the quantum mechanical phenomenon of tunneling. Theories of scanning tunneling microscopy aim to help understand experimental findings and thereby gain a deeper understanding of surfaces.

The principle of STM is to bring a sharp metallic tip close (a few Å) to the surface. With applying of a bias voltage between tip and sample a tunneling current (0.01 nA-50 nA) will flow between them. The Image contrast represents the difference in the tip-surface current at different surface sites. In this work the constant current mode of STM is used.

In the constant current regime of operation the position of the tip above the surface is adjusted such, that the tunneling current remains constant. The measured height of the tip above the surface is transformed in pixel intensity rendering a two-dimensional image of the surface. The tunneling current is highly influenced by the distance between sample-tip and the electronic structure of the sample.

STM yields information about empty and filled states of the sample. At negative tip bias empty states of the sample are probed, since the Fermi level of the tip lies higher than the Fermi level of the sample (cf. Fig. C-8-a). At positive tip bias the situation is reverse - the Fermi level of sample lies higher and the current flows from the filled sample states to the tip, i.e. the filled states of the sample are probed, Fig. C-8-b .

There are several theories on STM [171–173] containing different levels of sophistication. The most simple theory by Tersoff and Hamman [174, 175] is based on a perturbation approach as described by the Bardeen transfer-Hamiltonian [176]. This model shows that the tunneling current is proportional to the surface local density of states at the Fermi level energy and at a given tip position. The tip is modeled as a locally spherical potential well where it approaches nearest to the surface. The effect of the tip on the tunneling current is neglected in this model.

The tunneling current is proportional to :

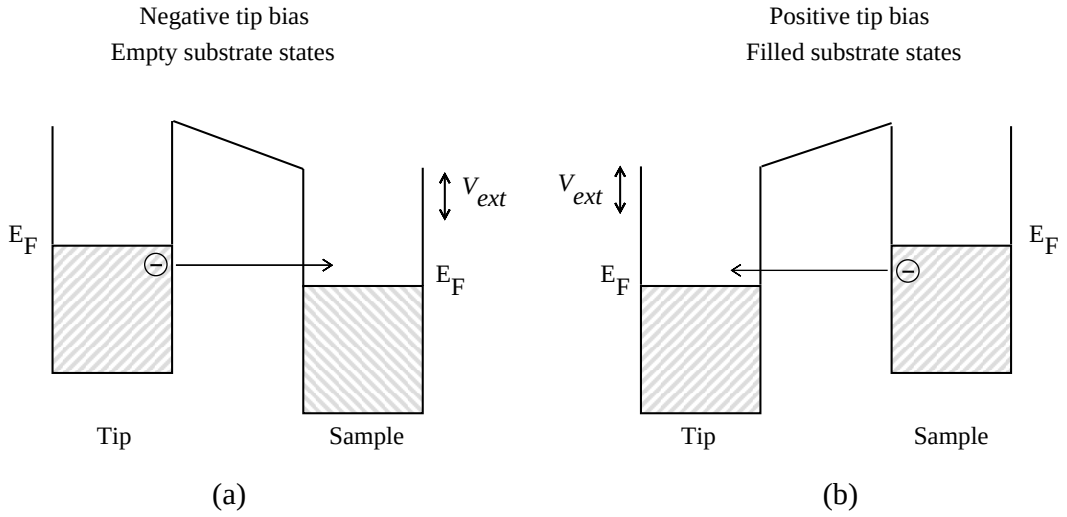

Fig. C-8: The negative tip bias probes empty substrate states (a) and positive tip bias probes filled states of the substrate (b).

$$I(R) \propto \sum_{E_n=E_F-eV}^{E_F} |\psi(\vec{\mathbf{R}}, E_n)|^2 = eVn(\vec{\mathbf{R}}, E_F) \tag{C-1}$$

where I is the tunneling current, E_n the eigenstates of the crystal electrons, E_F the Fermi level, V the bias voltage. The probability of an electron in the state ψ at E_ψ to tunnel into a state χ at E_χ is given by the "Fermi golden rule"

$$W = \frac{2\pi}{\hbar}|M|^2\delta(E_\psi - E_\chi) \tag{C-2}$$

The tunneling matrix (Bardeen matrix), M, is given by an integral over the separation surface S between sample and tip.

$$M = \int_S (\chi^*\nabla\psi - \psi\nabla\chi^*) \cdot d\vec{\mathbf{S}} \tag{C-3}$$

The probability of tunneling is large for electrons close to the Fermi level having lower barrier.

$\delta(E_\psi - E_\chi)$ means that an electron can only tunnel if there is an unoccupied state with the same energy at the other side. In case of positive (negative) tip potential the occupied (unoccupied) states generate the current. Therefore by applying the alternating voltage, a completely different image scan be detected.

Thus, by applying a bias voltage V and considering the tip as a small perturbation of the system, the tunneling current at low bias and temperature is defined as:

$$I = \frac{4\pi e}{\hbar}\int_0^{eV} \rho_s(E_F - eV + \varepsilon)\rho_t(E_F + \varepsilon)|M|^2 d\varepsilon \tag{C-4}$$

Hence the current is given by combinations of the local density of states of the sample and the tip, weighted by tunneling matrix, M.

The clean Si(001) surface has been extensively studied by STM [98, 105, 106]. In STM images of the (2×1) structure, the silicon dimer appears symmetric at room temperature due to the time averaging of the flipflop motion of the buckled dimers. Low temperature images show the stable configurations to be the $c(4\times 2)$ and $p(2\times 2)$ structures consisting of asymmetric dimer rows [110, 177]. At low temperature (4.2 K), it has been demonstrated that a phase change between the $c(4 \times 2)$ and the $p(2 \times 2)$ can be induced by controlling the sample bias voltage [106].

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