

# Chapter 97

## Scanning Tunneling Microscopy

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Surface electronic states · Atom manipulation

### 97.1 Principle

STM is a surface microscope with extremely high spatial resolution, which enables us to *see* atoms on surfaces. When a sharp metal needle is located at a very proximate distance ( $\sim 1$  nm) from the sample surface (left panel in Fig. 97.1), tiny amount of electrical flow, called a tunneling current, is induced between them. Since the current is so sensitive to the variation in the tip-sample gap distance, atomic-scale surface corrugation can be detected by monitoring the current during the lateral scanning of the tip over the surface.

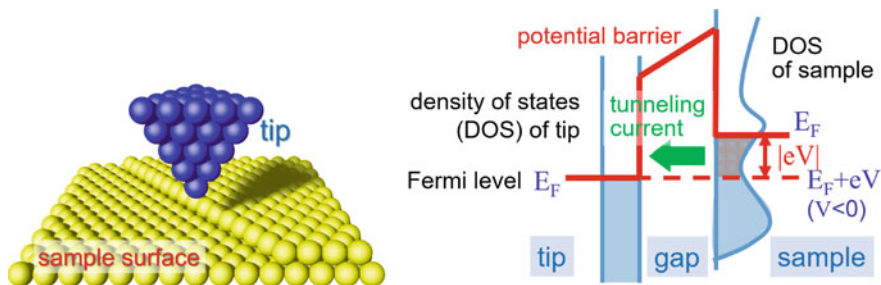
The tunneling current, which originates from quantum mechanics, is due to the overlap of the wave functions of the probe tip and sample surface. Since both wave functions decay rapidly in the gap region, the amount of the overlap and thus the tunneling current change drastically with the gap distance. A simple calculation tells us that the tunneling current is proportional to  $\exp(-10z\sqrt{\Phi})$ , where  $z$  (nm) is the gap distance between the tip and sample and  $\Phi$  (eV) is a potential barrier height or (averaged) work function. Using a typical number of  $\Phi$  (5 eV), the current is found to change by an order of magnitude with the gap-distance variation of 0.1 nm, which is less than typical atomic size.

Since the tunneling current is closely related to the wave functions, or electronic states, STM images also reflect the spatial distribution of the electronic states of the sample surfaces. According to the Tersoff–Hamann theory, STM image is a spatial mapping of the amplitude of surface wave functions whose energy is around the Fermi level. Usually, the wave function has a large amount of amplitude around surface atoms, and therefore, the atomic structure can be observed in the STM

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**Fig. 97.1** (left) Schematic of the tip and sample in STM. (right) Potential diagram for electron tunneling between the tip and sample surface

image. But some adsorbates are observed dark in the image when they reduce the wave function amplitude there.

With the negative bias voltage applied to the sample, STM probes the wave functions of the sample whose energy level is below the Fermi energy (filled states, right panel in Fig. 97.1), whereas the states above the Fermi energy (empty states) can be probed by the positive sample bias voltage. Because of the polarity dependence, STM images taken at both polarities look different, in particular, on semiconductor surfaces (e.g., Figure 97.3).

In more quantitative description, electronic states whose energy level is between the Fermi energy  $E_F$  and  $E_F + eV$ , where  $V$  is the bias voltage applied to the sample, contribute to the tunneling current and STM images (right panel in Fig. 97.1). In other words, the tunneling current is proportional to the integral of the local density of states in the energy range. When the bias voltage is raised so that the integral range covers the energy level of surface states, the contrast of the STM image may change drastically reflecting the newly involved states (e.g., Figure 97.4). The electronic sensitivity of the tunneling current also makes STM a local probe of surface electronic states with atomic-scale spatial resolution, whose function is specifically called scanning tunneling spectroscopy (STS).

Since STM utilizes the tunneling current as a probe, the sample has to be conductive electrically. STM cannot be used for the characterization of insulating materials.

## 97.2 Features

- Visualization of surface atomic structure.
- Observation of surface morphology with atomic-scale spatial resolution.
- Local probing and spatial mapping of surface electronic states around the Fermi level.
- Manipulation of atoms and molecules on surfaces for nanofabrication.

- Investigation of local excitation and response on surfaces by electrical field and/or current.

### 97.3 Instrumentation

In order to precisely control the gap distance between the probe tip and sample surface and scan the tip over the surface, the tip is mounted on a piezo-actuator with which one can precisely control the tip position in the xyz directions through an application of voltages on it. In usual STM imaging mode, which is often called constant current mode, the gap distance is feedback-controlled with the applied voltage on the piezo so that the tunneling current is kept constant. In this mode, the height information for the image is obtained by monitoring the piezo-voltage.

The maximum span of the piezo is  $\sim 1 \mu\text{m}$ , which indicates that the tip has to be brought within the range by other methods. Several coarse approaching mechanisms, such as Pan-type, Besoke-type, which are named after the inventors' names, and various types of inertial sliders, have been developed. The design of the STM unit basically depends on which type of coarse approaching is employed.

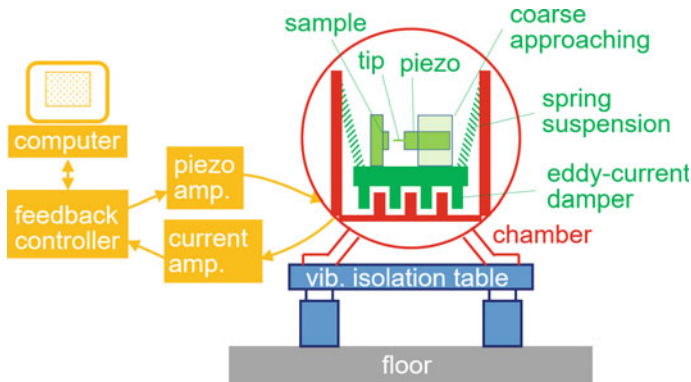
In order to achieve high performance of STM, mechanical and electrical noises have to be minimized. Designing the compact STM unit to achieve high resonance frequency between the tip and sample is crucial to suppress low-frequency vibrations from outside. A whole system is situated on a vibration-isolation table. A spring suspension system, an elastomer (e.g., Viton) stack, and an eddy-current damper are often used inside the chamber for the vibrational suppression (Fig. 97.2).

Since the amount of tunneling current is typically  $< 100 \text{ pA}$ , significant care should be taken to its noise level, and appropriate shielding has to be installed on the current line if necessary. The electrical noise in high voltage amplifiers that drive the piezo-actuator sometimes limits the performance and should also be cared.

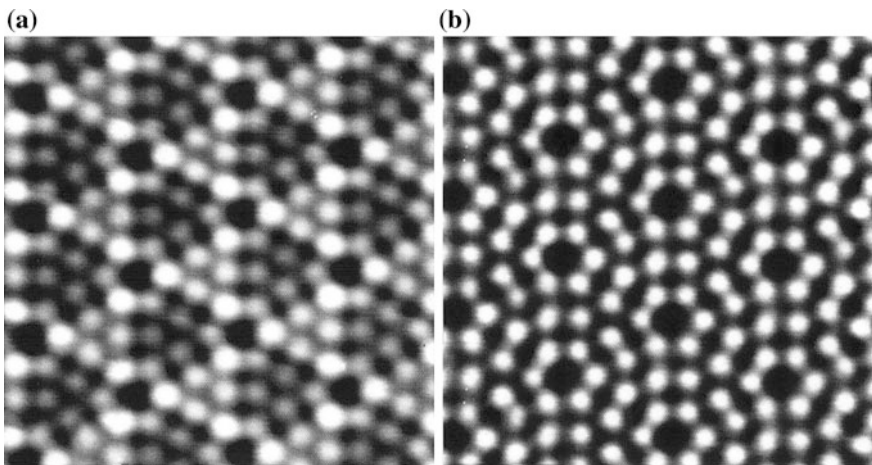
### 97.4 Applications

#### 97.4.1 *Atomically Resolved Imaging of the Si(111)7 x 7 Surface*

Since the observation of  $1/7$  ordered spots in an electron diffraction pattern, atomic structure of the Si(111)7 x 7 reconstructed surface had been a long-standing unsolved issue in surface science community until Binnig, Rohrer et al. [1] observed the atomically resolved real-space image of the surface with STM. The first STM image showed 12 protrusions in the rhombus unit cell and revealed inhomogeneous contrasts between the two triangular halves, indicating the



**Fig. 97.2** Schematic of STM instrumentation



**Fig. 97.3** STM images of the Si(111)7 x 7 surface taken with the sample bias voltage of negative (a) and positive (b) polarities

existence of 12 adatoms and stacking fault within the unit cell, respectively. Later, detailed analysis confirmed that the reconstructed structure can be described well by a dimer–adatom–stacking fault (DAS) model proposed by Takayamagi et al. [2].

Figure 97.3 shows typical STM images taken on the Si(111)7 x 7 surface by negative (a) and positive (b) sample bias polarities, implying (a) and (b) correspond to a spatial mapping of filled and empty states of the surface, respectively. In both images, 12 silicon adatoms, which are separated by 0.77 nm, are clearly resolved in the rhombus unit cell. Whereas all adatoms look similar in the empty-state image (b), in the filled-state image (a), the adatoms in the left-pointing triangles look brighter than those in the right-pointing triangles. The contrast difference can be explained by the difference in electronic states, and it is indeed due to the presence

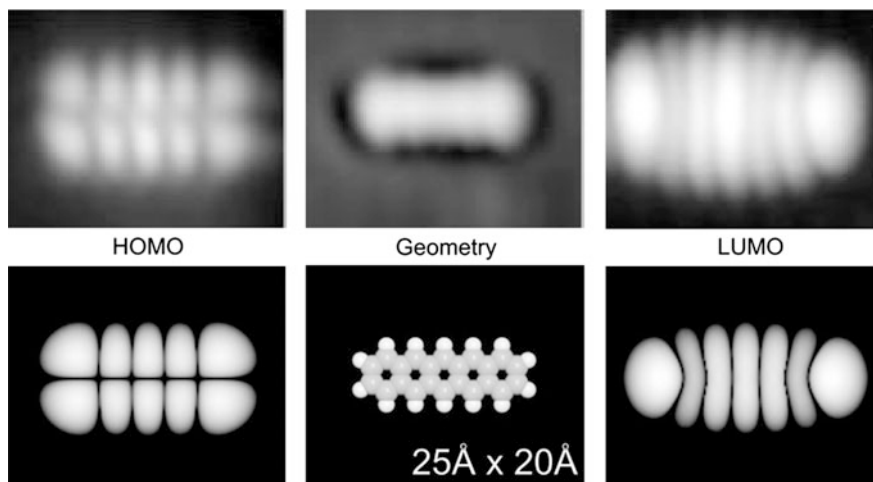
of stacking fault in the left-pointing halves (faulted half). A careful observer may notice that within the triangular halves the adatoms located at the corner (corner adatoms) look brighter than those at the center (center adatoms). These are also due to electronic origin and can be explained by the amount of electron donation from the adatom to neighboring rest atoms.

### 97.4.2 Imaging of Molecular Orbitals

STM provides us not only the atomic structure of the sample surface but also the spatial mapping of its electronic states. Here, imaging of molecular orbitals is presented as an example of the electronic state observation [3].

As mentioned in principle, an STM image corresponds to a spatial mapping of electronic states whose energy levels are in a range of the Fermi level  $E_F$  to  $E_F + eV$ , where  $V$  is the applied sample bias voltage. In the case of a single molecule, the energy levels of the electronic states are discrete, and the filled and empty states nearest to the Fermi level are called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. As shown below, one can obtain the spatial mapping of HOMO and LUMO states of a molecule by setting the bias voltage so that the energy level of the state is situated within the probing range.

Figure 97.4 shows STM images taken on a pentacene molecule adsorbed on a substrate. Since direct molecular adsorption modifies the molecular orbitals through



**Fig. 97.4** (top) STM images of a pentacene molecule taken with the sample bias voltage of -2.5 V (left), +0.5 V (center), and +1.8 V (right). (bottom) Calculated HOMO (left) and LUMO (right) states of a free pentacene molecule. Reprinted with permission from ref. [3]. Copyright 2005 by American Physical Society

the hybridization with the electronic states of the substrate, the observed molecule is situated on an atomically thin insulating layer (NaCl) formed on a metal substrate (Cu(111)). The top-left STM image was taken with the sample bias voltage of  $-2.5$  V. Since the energy level of the HOMO state is  $-2.4$  eV from  $E_F$ , which is within the probing range of  $E_F$  to  $E_F - 2.5$  eV, the spatial mapping of the HOMO state is imaged. A characteristic pattern showing a node along the long axis and 4 nodes along the short axis of the molecule, which are expected from a theoretical calculation (left bottom), is clearly observed.

## References

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