Chapter 1
Introduction

In many areas of science and technology there is a trend toward the nanoscale or even the atomic level. For instance, electronics is already undergoing a transition from microelectronics to nanoelectronics. As transistors with critical dimensions close to the single digit nanometer range are now in production, consumer PCs are become real nanoelectronic devices. Also in many other areas the progress toward the nanoscale is under way.

An additional reason for the trend toward the atomic scale is that material properties are ultimately determined by the atomic structure. In order to understand material properties it is necessary to go down to the nano or atomic scale. However, since the atoms are very small 50 years ago most people thought that it will probably never be possible to have direct access to materials on this scale (Fig. 1.1).

The "grandfather" of nanoscience and nanotechnology was R.P. Feynman. In a visionary talk in 1959 he postulated the possibility of nanotechnology down to the very atoms. In his talk entitled "There is Plenty of Room at the Bottom" he did not use the word "nanotechnolgy" since it had not been coined but he had the idea. This was very visionary in 1959 and he was not really certain so he phrased his vision in rhetorical questions and added some conditions. He reassured himself with his words:

> But I am not afraid to consider the final question as to whether, ultimately – in the great future – we can arrange the atoms the way we want; the very atoms, all the way down!
>
> … when we have some control of the arrangement of things on the small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do.
>
> What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them?

Feynman already saw the potential of nanotechnology already in 1959 before anyone else did. Now more than 50 years later it is interesting to see how many of his predictions have been realized. In some cases things have been realized in a much simpler fashion than he envisaged. To position things on the nanoscale he envisaged a cascade of machines of decreasing size, each driving the next smallest one. As was

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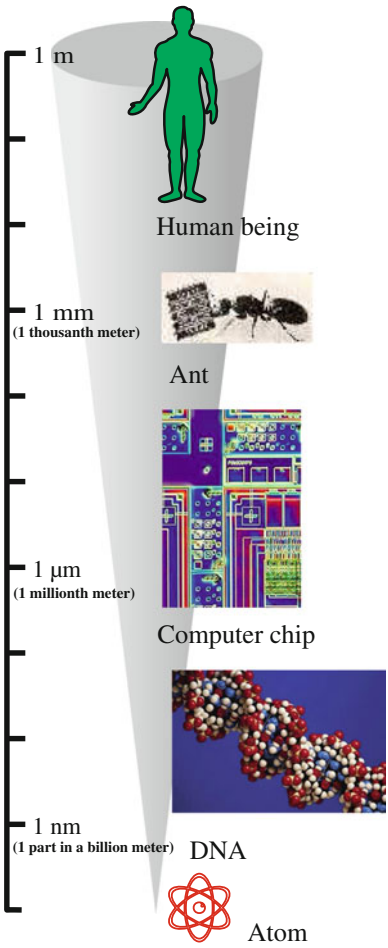

Fig. 1.1 Size scale from the human to the atom

discovered in 1990, it is possible to go all the way down to the nanoscale and build structures out of atoms in just one step from the macroscale to the atomic scale using a scanning tunneling microscope. The full 1959 speech is available on the internet.

Feynman envisaged that nanotechnolgy is possible in principle and would be very useful, but at that time the technology for imaging and controlling matter at the nanoscale had not been invented. With improvements in electron microscopy, it first became possible to image matter on the nanoscale. However, scanning probe microscopy is today a unique tool on the nanoscale, because it cannot only image but also structure matter on the nanoscale or even on the atomic scale. In scanning probe microscopy, a small probe is used to detect the local properties at a surface or interface down to atomic resolution. By scanning a grid of points on the surface, the detected properties can be mapped and are usually represented as an image. Because of the scanning mechanism, all these techniques are summarized as scanning probe

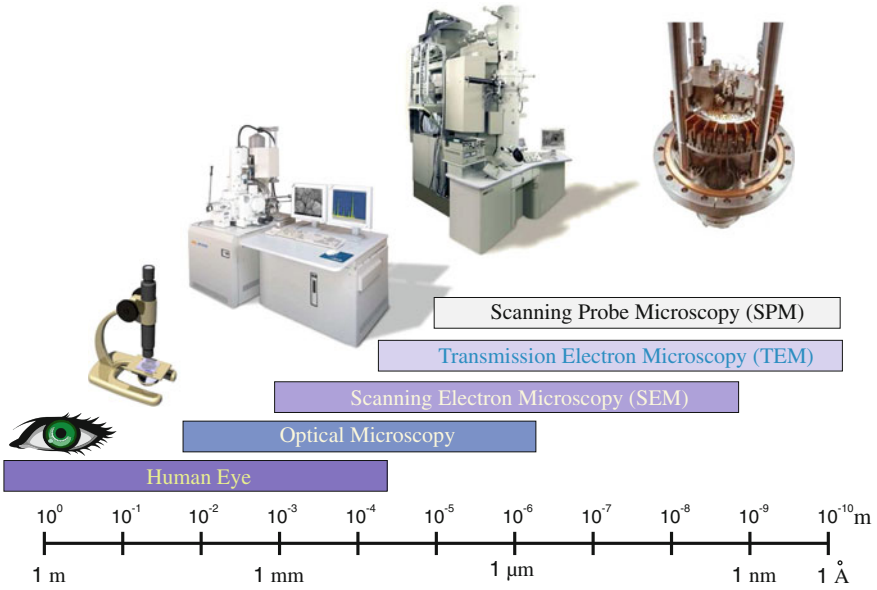

Fig. 1.2 Imaging ranges for different microscopy techniques in comparison

microscopes (SPM). If the interaction between the probe tip and the substrate is strong enough the substrate can be modified on the nanoscale.

One important figure of merit in microscopy is the resolution. Figure 1.2 compares the imaging ranges of different types of microscopy. The resolution of the human eye reaches down to one tenth of a millimeter. Optical microscopy reaches to slightly better than one micrometer due to the limitations set by the wavelength of visible light. Scanning electron microscopy (SEM) reaches to about one nanometer. Transmission electron microscopy (TEM) is capable of a resolution in the atomic range as are the various types of scanning probe microscopy.

While the resolution limit is important in microscopy also other characteristics are essential. For instance, the time to obtain an image, the contrast mechanisms (topography, chemical contrast …), the surface sensitivity, the working environment (ambient, vacuum, liquid …), and last but not least the price of the microscope. Each microscopy technique has its advantages and disadvantages for a particular application. For instance, if surface sensitivity is required SPM with its excellent surface sensitivity is the method of choice. If, however, features below the surface are to be imaged then TEM is the method of choice. If quick imaging within a few minutes down to the nanoscale is required then SEM should be used.

1.1 Introduction to Scanning Tunneling Microscopy

Today the scanning probe microscope is a very important tool in nanoscience. The principle of scanning probe microscopes is to move a sharp tip close to a surface in order to measure various properties with a spatial resolution on the nanometer or even atomic scale. The first kind of scanning probe microscope, the scanning tunneling microscope, (STM) was invented in 1981/1982 by Binnig and Rohrer who received the Nobel prize in physics 1986 for this invention. The most striking property of this kind of microscope is that it provides resolution down to the atomic scale in real space (Fig. 1.3b).

Here is an analogy which shows the precision of an STM working with atomic resolution. Such instruments are about 10 cm in size and can image with a resolution of about 1 Å, corresponding to a precision of about 10^{-9} of its size. Scaling this precision of 10^{-9} up to macrosize dimensions would correspond to using a pencil 1,000 km in length to write letters from Cologne (Germany) in a notebook in Rome (Italy) with 1 mm resolution!

A schematic of an STM, with fine metal tip used as a probe, is shown in Fig. 1.3a. A voltage is applied between the tip and the (conducting) sample. The tip is approached toward the sample surface until a current flows. A current (the tunneling current) can be detected shortly before tip and sample come into direct contact. This happens at distances between tip and sample of the order of 0.5–1 nm. The tunneling current increases monotonously with decreasing tip-sample distance. Thus a certain measured tunneling current corresponds to a specific tip-sample distance. Since the tunneling current varies strongly (exponentially) with the tip-sample distance this

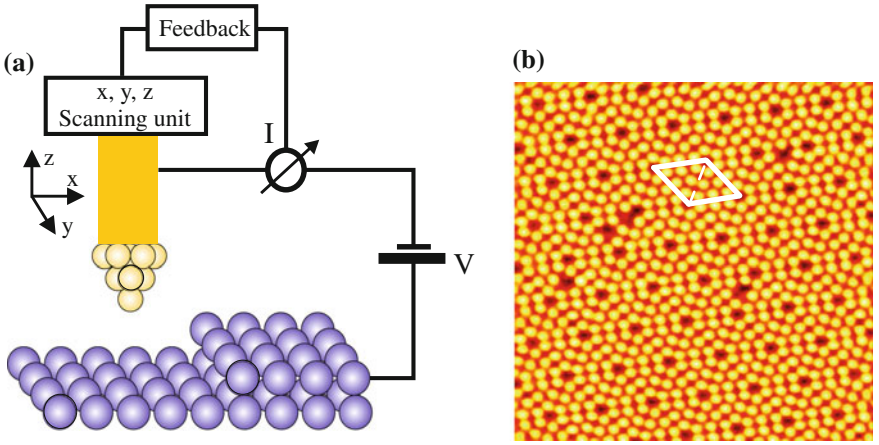

Fig. 1.3 **a** Schematic of a scanning tunneling microscope (STM). **b** STM image of the Si(111) surface. Individual atoms are observed as *yellow dots*. The rhombic unit cell is indicated by *white lines*. Besides the periodic arrangement of the atoms also defects such as single missing atoms can be observed

quantity can be used to measure (and control) the tip-sample distance very precisely. We will see later that a 20 % change in the tunneling current corresponds to a change in the tip-sample distance of only 0.1 Å. The tip is positioned with such high accuracy using piezoelectric actuator elements. The mechanical extension of this actuator elements is proportional to the voltage applied to their electrodes. In this way, the tip can be moved in x, y and z directions with sub-ångström resolution.

While the tip is scanned along the surface in x and y directions, a feedback mechanism constantly adjusts the tip height by approaching or retracting the tip to a tip-sample distance at which the tunneling current remains constant. If there is an atomic step at the surface, as shown in Fig. 1.3a, and the tip approaches this step edge laterally during scanning, the tunneling current will rise due to the smaller distance between tip and sample. As a reaction to this the feedback circuit will retract the tip in order to maintain a constant tunneling current, i.e. a constant tip-sample distance. Recording the feedback signal (tip height) as a function of the lateral position results in a map (or image) of the tip height, which often corresponds to the surface topography of the sample surface.

The interpretation of the tip height for constant tunneling current as the topography of the surface is a first approximation. So-called electronic effects can change this interpretation. A simplified example of this are atoms on a surface which have the same height (of their nuclei) but their electronic properties are different in the sense that one atom has a "higher electrical conductivity" than the other. The atom with the "higher conductivity" will appear higher (same tunneling current at larger tip-sample distances) while for the case of the "less conducting atom" the tip has to approach closer to maintain the same tunneling current.

Figure 1.3b shows an atomically resolved image of a Si(111) surface. Single silicon atoms are observed as yellow dots. The operation of an STM can be visualized experimentally by combining a scanning electron microscope (SEM) with an STM. The SEM can be used to image the motion of the STM tip during scanning. A movie of a scanning STM imaged during operation with an SEM can be accessed at http://www.fz-juelich.de/pgi/pgi-3/microscope.

The tunneling junction (sample-gap-tip) can be treated in different approximations. Here in the introduction, we consider a simple one-dimensional approximation for one electron tunneling in order to grasp the very important exponential dependence of the tunneling current on the tip-sample distance. Later we will look more deeply into the theory of STM.

In quantum mechanics, electrons in a solid are described by a wave function $\psi(\mathbf{r})$. In the free electron approximation the wave function of an electron of energy E is an oscillating function. The one-dimensional Schrödinger equation is solved by the (not normalized) wave function

$$\psi(z) \propto e^{\pm ikz}, \quad k = \sqrt{\frac{2m_e E}{\hbar^2}}. \tag{1.1}$$

When drawing such a wave function, it should be always remembered that the quantum mechanical wave function is genuinely a complex function, which is difficult to

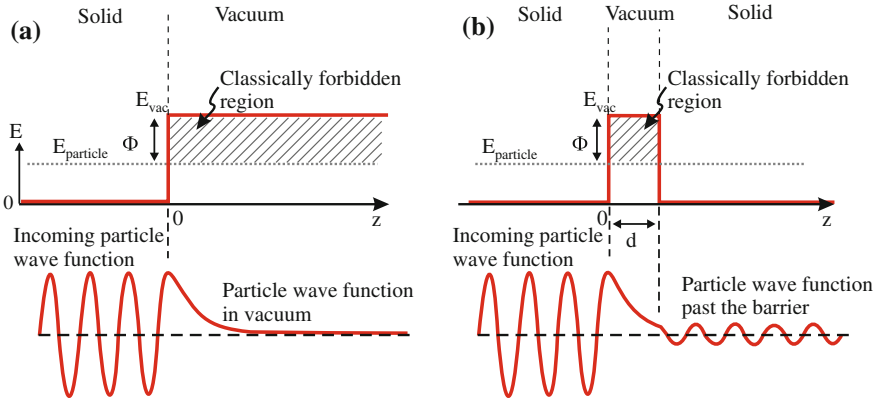

Fig. 1.4 **a** The *top graph* shows the potential diagram with a barrier of height Φ and the energy of an electron $E_{\text{particle}} = E_{\text{F}}$. The *lower graph* shows the real part of the electron wave function with an exponential decay of the wave function in the vacuum region. **b** The *top graph* shows the potential for a solid-vacuum-solid configuration. The *lower graph* shows the electron wave function oscillating in front of the barrier, exponentially decaying inside the barrier and again oscillating past the barrier

draw. Therefore, usually only the real or imaginary part is drawn, as in Fig. 1.4. The sinusoidal appearance of the real or imaginary part of the wave function should not make us forget that the absolute value $|\psi(z)|^2$ of such a wave function e^{ikz} has the constant value of one for all z.

In the following, we consider the electrons in a solid with the highest energy (at the Fermi level E_{F}) and call this energy the particle energy $E = E_{\text{particle}}$. The energy of these electrons at the Fermi level is lower than the energy of free electrons (the vacuum energy). This energy difference is roughly the bonding energy of the electrons inside the solid. If the Fermi energy were larger than the vacuum energy, the electrons would leak out of the solid toward the vacuum. The minimum energy needed to remove an electron from a solid is called the work function Φ, which is shown graphically in Fig. 1.4a.

Thus at a surface there is a barrier (work function) preventing the electrons from leaving the solid to the vacuum level E_{vac}. In classical mechanics, particles cannot penetrate into a barrier which is higher than their energy. In quantum mechanics, particles can penetrate into a region with a barrier higher than their energy. An ansatz with an exponentially decaying wave function inside the barrier (in the vacuum) as $\psi(z) = \psi(0)e^{-\kappa z}$ leads to a solution of the Schrödinger equation inside this potential barrier (Fig. 1.4a). The probability of a particle being at a position z inside the barrier is approximately proportional to $|\psi(z)|^2$

$$|\psi(z)|^2 = |\psi(0)|^2 e^{-2\kappa z}, \quad \kappa = \sqrt{\frac{2m_{\text{e}}\Phi}{\hbar^2}}. \tag{1.2}$$

If after some distance d the vacuum is replaced by another solid this configuration is already a one-dimensional model of the tunneling junction (electrode-gap-electrode). A potential diagram for such a tunneling barrier is shown in Fig. 1.4b. Since inside the solid the vacuum barrier is not present, the solution for the wave function is an oscillating wave, which is again a solution inside the second solid. This means that in quantum mechanics the electron has a finite probability in both metals. In the square barrier model a barrier, of height $\Phi = E_{\mathrm{vac}} - E_{\mathrm{F}}$ and width d is considered. In the course of the solution of the square barrier problem, the transmission coefficient for the wave function behind the barrier can be calculated. (This is usually done in the quantum mechanics course. We will come to this in a later chapter.) The probability of an electron being observed on the right side of the barrier is proportional to the absolute square of the wave function at the end of the barrier $|\psi(d)|^2$. A transmission coefficient T can be defined as

$$T = \frac{|\psi(d)|^2}{|\psi(0)|^2} \approx e^{-2\kappa d}. \tag{1.3}$$

The main characteristics are: the transmission coefficient decays exponentially with the tip-sample distance d and decreases exponentially with the square root of the work function. If we use the right electrode as the tip, the tip probes the probability density of the electron states at distance d from the surface. Later we will see that the tunneling current is proportional to the transmission coefficient.

Evaluating (1.2) using the free electron mass for m_{e} and a typical value for the work function of a metal ($\Phi \approx 4.5\,\mathrm{eV}$), 2κ is about $20\,\mathrm{nm}^{-1}$. Thus a variation of the barrier thickness of 0.1 nm results in a difference in the transmission factor of an order of magnitude ($\sim$7.4). Hence the tunneling current increases by about an order of magnitude if the tip approaches by one Å to the sample. This sensitivity in the tip-sample distance is the reason for the extremely high vertical resolution of the STM which can reach the picometer regime. Atoms on the tip which protrude only 2.5 Å ($\sim$one atomic distance) less toward the sample carry only a factor of 150 less current. This means that the majority of the tunneling current is carried by the "last atom", which also explains the very high (ultimately atomic) lateral resolution of the STM.

1.2 Introduction to Atomic Force Microscopy

One disadvantage of STM is that it can be used only for conducting samples since the tunneling current is the measured quantity. An atomic force microscope can also be used on insulating samples. The atomic force microscope (AFM) is alternatively known as the scanning force microscope (SFM). However, here we will use the more common name atomic force microscope. Instead of the tunneling current, which is the measured quantity in STM, in an atomic force microscope force microscopy the force between the tip and sample is measured. In Fig. 1.5, a qualitative sketch of the force between tip and sample is given. Three different regimes can be distinguished.