In EDS, all photons emitted by the sample are collected and measured simultaneously by a solid state X-ray detector. The common EDS detector is lithium-drifted silicon, Si(Li). Intrinsic or high purity Ge (HPGe) is also used, which is more common in the case ofTEM instruments due to their higher collection efficiency. When an X-ray photon falls on an intrinsic semiconductor (having no charge carriers), due to photoabsorption, charge carriers (electrons and holes) are created. These are swept by an applied bias forming a charge pulse. This charge pulse is then converted into a voltage signal. Intrinsic condition is hard to achieve and detector crystals are made to behave like intrinsic silicon. This is made by applying Li on *p*-type Si, thereby forming a p-n junction. The junction region will behave like an intrinsic semiconductor. The width of this region can be expanded by applying an electric field at elevated temperatures. The removal of most of the *p*-type Si region makes a detector (which is the Si left behind). However, the Li present is mobile at room temperature and it is necessary to cool down the detector to 77 K in order to operate the detector under bias.

The intrinsic silicon active layer is covered on the front side with *p*-type Si and in the back with *n*-type Si. The front is also coated with a thin gold layer for electrical contact. The device is kept behind a *Be* window which blocks visible light. Also, it mechanically seals the detector assembly from the vacuum chamber, thereby avoiding contamination. When an energetic photon strikes the detector, charge carriers are created. The detector is reverse-biased, i.e. *p*-type is connected to negative potential. This means that when the charge carriers are created, the holes move to the *p*-side while the electrons move to the *n*-side, thus creating a pulse of electrons at the *n*-side, which can be amplified. In order to reduce noise and also Li mobility, to maintain the intrinsic condition, the detector is cooled. When photons of high energy above the Si K shell binding energy (1.84 keV) fall on it, photoelectron emission takes place. The photoelectron loses energy inelastically, thus exciting electron-hole pairs. The core hole produced may be filled by photoemission or Aüger emission. The photon may be reabsorbed resulting in photoemission, or it may undergo inelastic scattering. Thus, all the energy of the initial photon is used in generating electrons. In favourable conditions, the number of charges created in the detector per photon is equal to photon energy/energy required for the creation of an electron-hole pair ($\varepsilon$). For a 5000 eV photon, this works out to 5000/3.86 or 1295 electrons ($\varepsilon$ at 77 K is 3.86 eV for Si). However, this number is very small, and generates a very small charge pulse of $2 \times 10^{-16}$ C. Each charge pulse, converted to voltage, represents the energy of the photons. The resolution of the photon energy, distinguishable by solid state detectors of this kind, is 130 eV at MnK$\alpha$ (5890 eV). The detector resolution is a function of X-ray energy and it is about 65 eV at 282 eV. There are several advanced detectors such as the silicon drift dectector, which works at 250 K, having the same resolution but an increased sampling rate. A microcalorimeter EDS works by measuring the temperature difference caused by the absorption of X-rays. With this, an increased energy resolution is possible, which is about 4.5 eV at MnK$\alpha$.

Wavelength dispersive spectrometers work on the principle of Bragg diffraction, $n\lambda = 2d\sin\theta$, where $\lambda$ is the wavelength of the X-ray and $\theta$ is the angle of incidence. Therefore, at various angles of incidence, it is possible to scatter rays of different wavelengths to the detector. As $\sin\theta$ cannot be larger than one, the longest wavelength diffracted is $2d$, therefore the crystal puts a limit on the range of elements covered. There are also other limitations of the hardware. When $\theta$ is 90°, the detector has to sit at the X-ray source; when $\sin\theta$ is close to zero, the movement of the crystal near the specimen is a problem. In order to diffract the low energy X-rays emitted by Be, B, C and N, it is necessary to use crystals of large $d$ values.

This is made possible by Langmuir–Blodgett films (see the chapter on Self-assembled Monolayers) whose interlayer spacing can be tuned by varying the chain length of the monolayer. Most of the measurements of long wavelength X-rays are done by layered synthetic microstructures. This contains evaporated alternate layers of heavy and light elements. The thickness of the layers can be easily controlled.

The detector commonly employed is a gas proportional counter. This has a gas mixture (typically 90 per cent argon, 10 per cent methane). The detector assembly has a thin window through which the X-ray photon falls in. It causes the ejection of a photoelectron, which is accelerated by the high voltage applied on the collector. The electron causes subsequent ionization in the gas and as a result, a gain factor of the order of $10^5$ is achieved. There have been numerous improvements in gas-filled detectors involving the use of improved windows, other gases, etc.

The spatial resolution of SEM is affected by the beam size as mentioned before. But the beam causes interaction with the sample and the region of interaction exceeds the physical dimension of the beam itself. The spatial extent increases laterally as well as depth-wise, and this interaction volume depends on the material and also on the beam energy. At large energies, the beam interacts to a greater extent, while the depth of interaction decreases with a decrease in electron energy till about 100 eV and at very low energies of the order of a few eV, it increases again. The range of interaction is decided by the electron attenuation length. The universal electron attenuation length of materials is given in Fig. 2.7. As seen in the figure, the attenuation length increases with electron energy and has a minimum at a few hundred eV. This makes it possible to design highly surface-sensitive SEMs by reducing the beam energy. This development is discussed in low energy SEM.

### 2.2.2 Transmission Electron Microscopy

In TEM, the transmitted electrons are used to create an image of the sample. Scattering occurs when the electron beam interacts with matter. Scattering can be elastic (no energy change) or inelastic (energy change). Elastic scattering can be both coherent and incoherent (with and without phase relationship). Elastic scattering occurring from well-ordered arrangements of atoms as in a crystal, results in coherent scattering, giving spot patterns. This can be in the form of rings in the case of a polycrystalline material. However, inelastic scattering also occurs, which also gives regular patterns as in the case of Kikuchi patterns. Inelastic processes give characteristic absorption or emission, specific to the compound or element or chemical structure. Because of all these diverse processes, a transmission electron microscope is akin to a complete laboratory.

There are two main mechanisms of contrast in an image. The transmitted and scattered beams can be recombined at the image plane, thus preserving their amplitudes and phases. This results in the phase contrast image of the object. An amplitude contrast image can be obtained by eliminating the diffracted beams. This is achieved by placing suitable apertures below the back focal plane of the objective lens. This image is called the bright field image. One can also exclude all other beams except the particular diffracted beam of interest. The image using this is called the dark field image (Fig. 2.8).

TEMs with resolving powers in the vicinity of 1Å are now common. As a result, HRTEM is one of the most essential tools of nanoscience. Interaction of the electrons with the sample produces elastic and

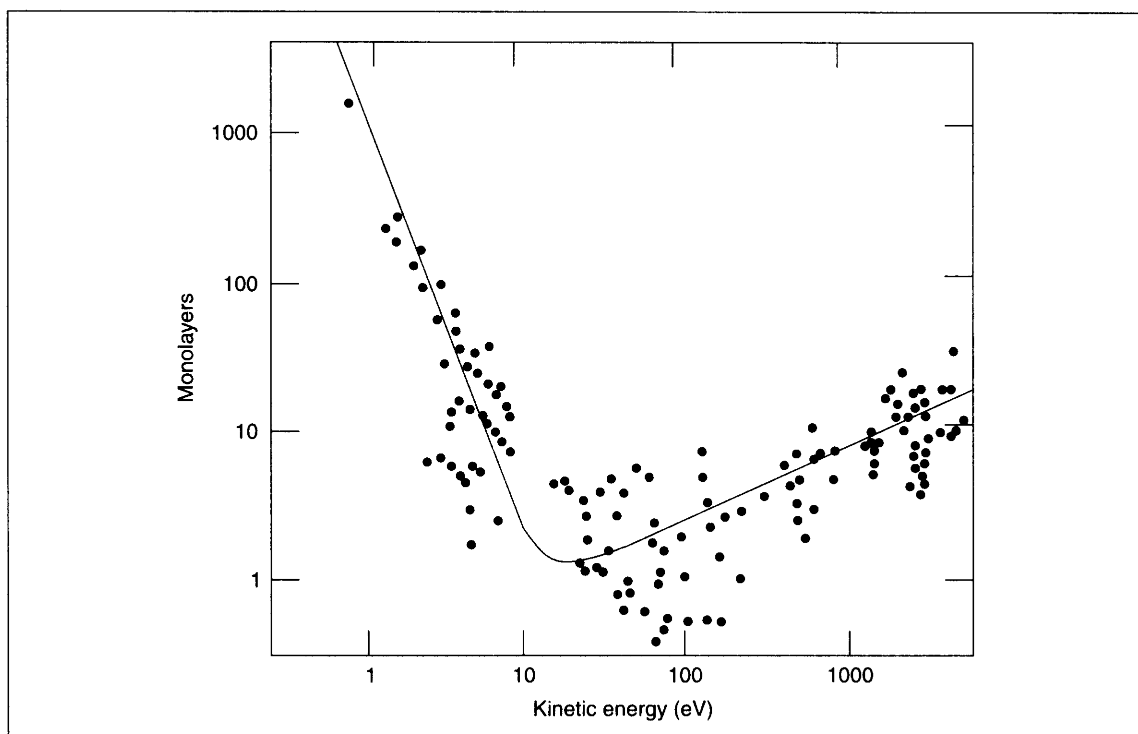



**Fig. 2.7:** *Universal attenuation length data of materials as a function of electron kinetic energy. At low kinetic energies, the electrons are sensitive to only a few monolayers of the material. The data points correspond to the experimental data from a number of materials and the line is an approximate fit.*

inelastic scattering. Most of the studies are done with the elastically scattered electrons which form the bright field image. The inelastically scattered electrons are used for electron energy loss spectroscopy as well as for energy filtered imaging. Electrons emerging from the sample, after a series of interactions with the atoms of the target material, have to be transferred to the viewing screen to form an image. This is greatly influenced by the transfer characteristics of the objective lens. A parameter which can be used to understand the transfer properties is the phase contrast transfer function (CTF). This function modulates the amplitudes and phases of the electron diffraction pattern formed in the back focal plane of the objective lens. The function is given as:

$$T(k) = -\sin\left[\frac{\pi}{2}C_s\ \lambda^3 k^4 + \pi\,\Delta f\,\lambda\, k^2\right],$$

where, $C_s$ is the spherical aberration coefficient, $\lambda$, the wavelength of the beam, $\Delta f$, the defocus value and $k$, is the spatial frequency. Defocus setting (with reference to the Gaussian focus) in the electron microscope determines the shape of the CTF. This is given in Angstrom units. In the electron optical

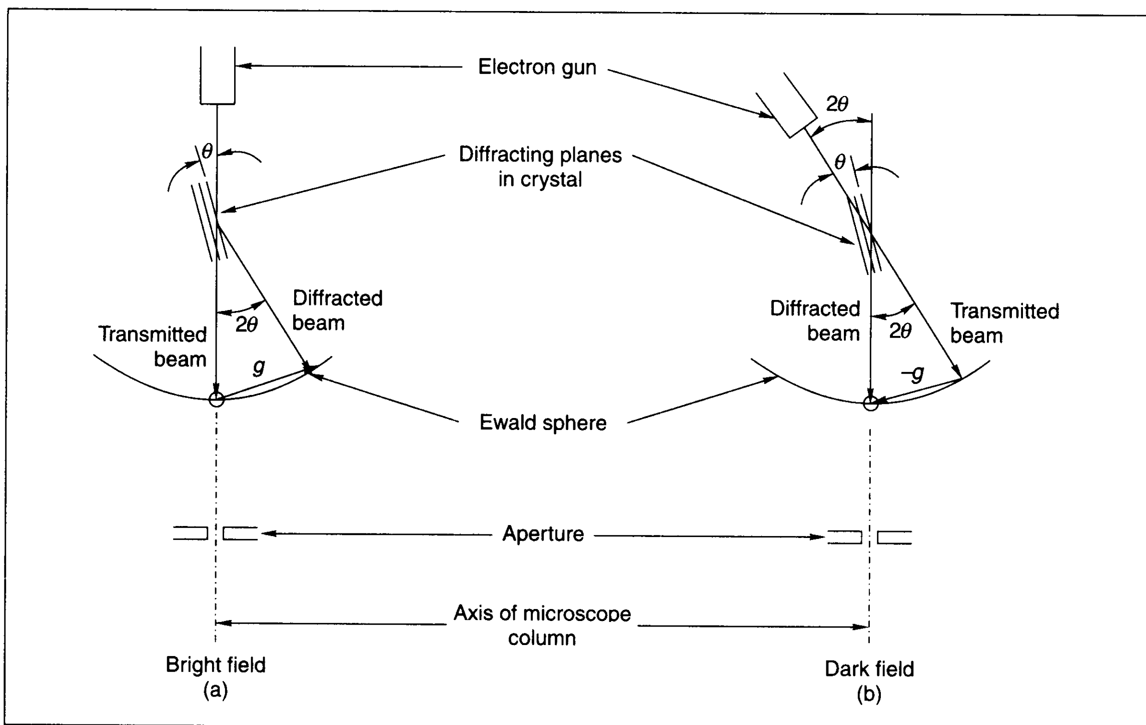



**Fig. 2.8**: *Two kinds of image collection: (a) bright field, and (b) dark field. In bright field, the transm itted beam is used for imaging. In dark field, the diffracted beam is used for imaging. The diffracted beam can be used for imaging either by using a movable aperture or by shifting the incident beam, keeping the aperture constant. Adapted from Thomas and Goringe, 1979 (Ref. 2).*

convention, over-focus implies negative defocus values, while under-focus (the only useful range) implies positive defocus values. The CTF of a 200 keV microscope will look like the one shown in Fig. 2.9.

The general characteristic to be noted is its oscillatory nature. When it is negative, we have a positive phase contrast and atoms will appear dark on a bright background. When it is positive, a negative phase contrast occurs, and atoms will appear bright on a dark background. When it is equal to zero, there is no contrast or information transfer. CTF can continue forever but it is modified by functions known as 'envelope functions' and eventually dies off.

In any instrument, the most important aspect is the resolution. This is the ability of the instrument to discriminate between two closely lying objects. As the wavelength of electrons is in the picometer range, it is only natural to expect a resolution of that order. However, this is not the case. This is because of the fact that electron lenses have aberrations and also due to the fact that it is impossible to get a coherent electron beam. We can express the resolution as, $d \alpha C_s^{1/4} \lambda^{3/4}$.

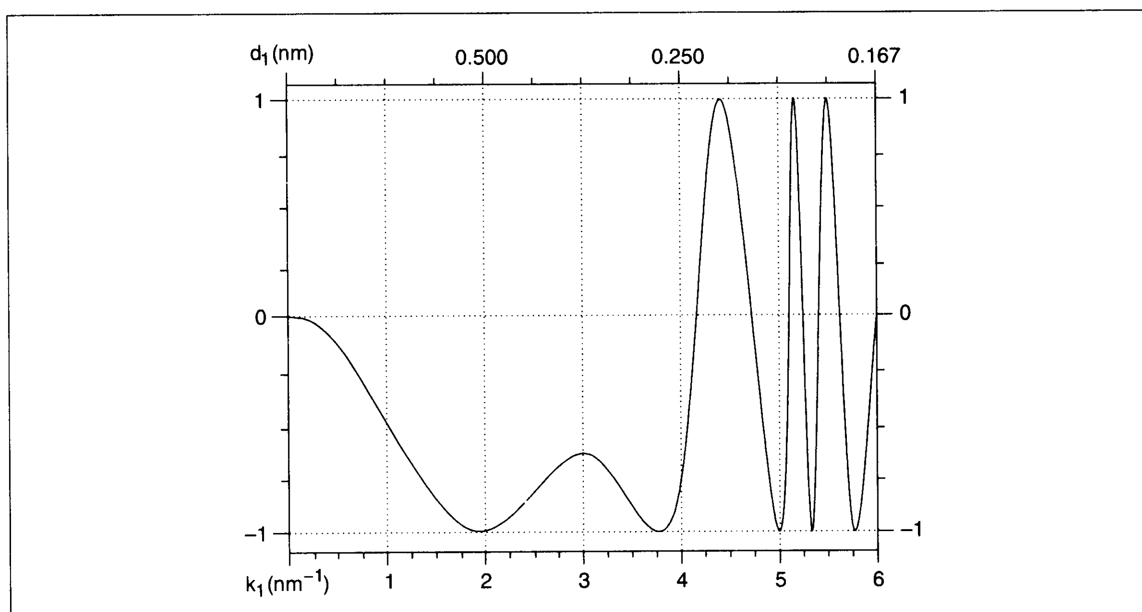



**Fig. 2.9**: *A contrast transfer function.*

The interpretable resolution, or the structural or point resolution is the first zero crossover of the CTF at the optimum defocus. This can be given as $\delta \sim 0.66(C_s\lambda^3)^{1/4}$. $C_s$ increases with electron beam energy, but the point resolution improves with acceleration voltage as $\lambda$ is reduced. $C_s$ ranges from 0.3 mm for 100 keV to 1.5 mm for 1 MeV. The resolution changes from 0.25 to 0.12 nm. In view of the increasing cost of the instrument at larger acceleration voltages and irradiation damages at larger acceleration voltages, it is more advisable to use intermediate energy ranges. The instrumental resolution is lesser than this value, but if one knows the defocus and $C_s$ accurately, one can obtain improved images by subsequent processing. The lattice resolution refers to the finest lattice spacings observable in images. The lattice images may not provide better information about the sample in several cases as far as the local atomic environment is concerned. Interpretable and instrumental resolutions are important in assessing the performance of the instrument.

## 2.2.3 STEM

STEM is a hybrid instrument with the features of both SEM and TEM. The same probe beam in TEM can be demagnified and used as a probe beam, which can be scanned over the sample. The probe beam has to be small and bright and therefore, field emission sources are needed to obtain beam dimensions that are smaller than a nanometer. The principal components of STEM are shown in Fig. 2.10. The beam coming off the gun is demagnified by the objective lens. A set of condenser lenses is placed above the objective lens to add flexibility to the beam parameters. The scanning coils are incorporated into the objective lens

itself. The beam falling on the sample produces a diffraction pattern. The pattern is a convergent beam electron diffraction and is also called electron nano diffraction. The beam size is close to the resolution limit of the instrument. The observation screen may have an aperture and some part of the transmitted beam is used for electron energy loss spectroscopy (EELS, see below). This analysis is usually done with the central part of the beam (Fig. 2.10(a), bright field), but can also be done with any of the diffracted spots (Figs 2.10(b) and (c)). That is, the dark field images may be formed either by the deflection of the diffracted beam into a centrally placed objective aperture, or by the displacement of the aperture which allows only a specific diffracted beam to pass through. The measurement may correspond to either the EEL spectrum or an image using electrons with characteristic energy loss. The normal bright field image is made with no-loss electrons from the central beam. Dark field images are made with electrons deflected from the beam axis with or without energy loss. Deflection coils placed after the sample are used to direct the chosen part of the diffraction pattern to the entrance aperture of the spectrometer. Common dark field STEM images are collected by imaging part of the diffraction pattern outside the central beam spot.

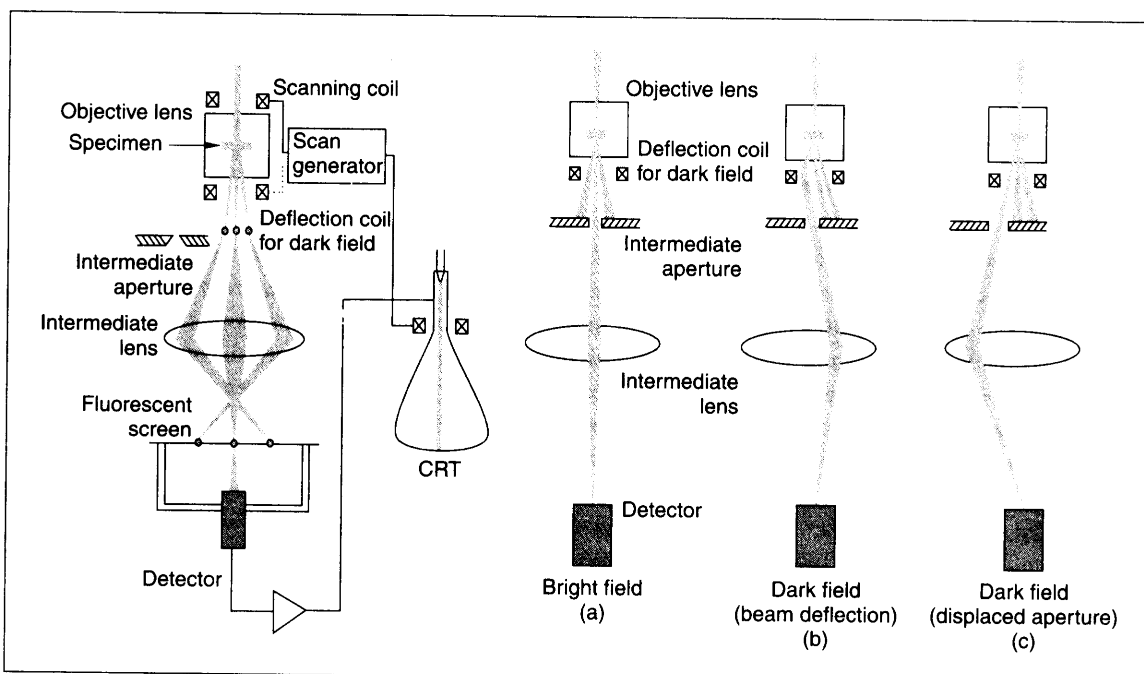



**Fig. 2.10:** *Schematic of a STEM instrument and various ways of operation of the same. Adapted from Thomas and Goringe, 1979 (Ref. 2).*

Detectors can be placed around the sample to detect the secondary radiations coming out from the sample. X-rays, secondary electrons and Aüger electrons can be analyzed, with the last two normally being used for imaging purposes and the first one for microanalysis. In microanalysis, the important aspect to be noted is that since the sample thickness is small in STEM, the interaction volume is very small. The

chemical analysis of small volumes is limited only by the quality of the signal obtained as far as an X-ray is concerned. A combination of ELS and X-ray analysis may be used in most cases.

There are numerous areas where STEM can be of use in nanotechnology. With the current instrumental resolution of the order of 0.1 nm, complete characterization of materials up to 1 nm is possible. Diffraction of objects at 1 nm is possible. All kinds of materials such as crystalline, amorphous and biological materials have been investigated. With a growing need to know everything about a nanostructure, applications of STEM are also likely to increase.

## 2.2.4 Image Collection in Electron Microscopes

In SEM, the image is collected in a video monitor (CRT), which is captured by a camera or a computer. In TEM, the image is formed when transmitted electrons fall on a phosphor screen. The image formed can be photographed. Photography is a result of a series of chemical reactions. This uses the light sensitivity of silver halides. While silver bromide is commonly used, iodide and chloride are also used. When the grains of silver salt present in a gelatinous film are impinged with photons, they reach an activated state, which get reduced by a reducing agent (developer). The reduction will ultimately happen on all the silver halide grains, including those which are not exposed to photons. As a result, one needs to stop the process of reduction. This is done by putting the film in water. The remaining silver grains can still get reduced later on. In order to avoid this, these grains have to be removed by a process called fixation for which thiosulphate is used. After the process of development and fixation, the film is dried and stored.

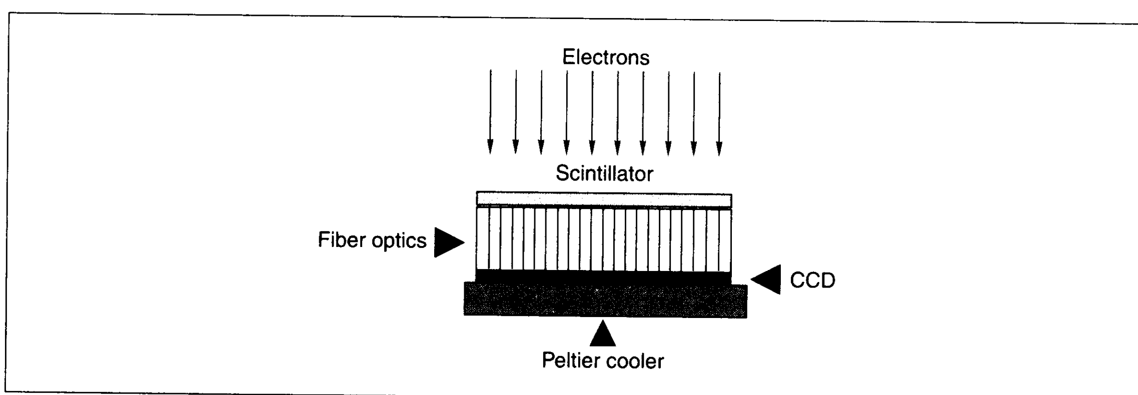
Basically two types of emulsions are used in photographic films. The classification is based on light energy. Panchromatic emulsions are sensitive to all wavelengths and are therefore handled in total darkness till fixation. Orthochromatic emulsions are sensitive to certain wavelengths only. There is a safe light in which it can be handled. The film has two characteristics. Light sensitivity, which decides the length of the exposure time and grain size, which determines the extent to which one can enlarge the image. The extent to which the film is darkened depends on the light intensity and duration of exposure. These parameters have to be optimized for a given film.

### Digital Imaging in TEM

In digital TEM imaging, the image formed by the electron beam is captured by a charge-coupled device (CCD). CCD is an image sensing device, in which an array of light sensitive capacitors is connected on an integrated circuit. By external control, the charge at one of the capacitors can be transferred to another. Depending on how the CCD is implemented, there are three common kinds of architectures. In the 'full-frame' CCD, the charge is collected on all the available area of the CCD and the information is read out by placing a mechanical shutter over the sensor. In the 'frame-transfer' CCD, half of the image area is covered with an opaque mask and the image collected is transferred immediately to the opaque area and read out slowly. As double the area (sensor and intermediate storage) is needed, this adds to cost. But quick accumulation of image becomes possible by this way. In the 'interline' architecture, every other column of the sensor is masked and the image is shifted only one pixel after collection. This adds to a fast shutter

speed and smearing of the data is less, but only half the area is effectively used and so the fill-factor is only half. There are ways to improve this, however.

In the CCD detectors used in TEM, the photons have to be generated first. For this a scintillator plate is used. The electrons fall on this and photons are generated. The photons are transferred to the CCD by fiber-optics. At the CCD photons generate charges and they are read out, pixel by pixel. CCDs are generally cooled to reduce the noise (dark current).




**Scheme 2.1**: *Schematic of a CCD detector used for TEM.*

## 2.2.5 Environmental Transmission Electron Microscopy (ETEM)

Science at the nanoscale is concerned with the variation of properties with size and shape. Structural and morphological changes occur in these materials with minor changes in temperature and other parameters such as atmosphere. Because of these reasons, nanomaterials have to be studied at higher pressures and temperatures. Such studies have been important in areas such as catalysis. Gas–solid interactions, in general, have been of interest in areas such as corrosion, oxidation, etc. Biological materials need to be investigated close to their natural environments. All these requirements have necessitated the modification of conventional TEMs to work at modified conditions. These microscopes are called environmental transmission electron microscopes. They facilitate the investigation of structural and chemical changes on materials upon gas–solid and liquid–solid interactions at varying temperatures.

In ETEM, the sample is confined in a high pressure region, as high as 150 torr, in such a way that the column vacuum does not deteriorate significantly. The key instrumental feature is an environmental cell in which the pressure–temperature conditions are regulated. This can be done by using two kinds of approaches: 1. using electron transparent windows to confine the system under investigation, and 2. using differential pumping to confine the system. The window method has an advantage in that it makes higher pressures possible, but it is difficult to get high resolution due to the additional scattering as a result of the window material. Due to the space requirements of such a cell, these kinds of cells have been used only in

high energy instruments because of their larger pole-piece gaps. The medium energy TEMs today have pole-piece gaps of 7–9 mm, large enough to accommodate a cell. Differentially pumped cells are used nowadays.

Such instruments are used for the *in-situ* synthesis of nanoparticles, the study of carbon nanotube growth, *in-situ* chemical transformations of nanoparticles, etc. Combining diffraction, microscopy and elemental analysis in ETEM facilitates complete investigations as a process occurs. It is possible to make nanolithographic structures in such an instrument.

## 2.2.6 Electron Energy Loss Spectroscopy at the Nanometer Scale

The characterization of materials at the nanometer scale is central to nanoscience and technology. With improvements in electron sources and optics, it is possible to generate beams of sub-nanometer spatial spread, which can probe into the chemical and structural aspects of the sample. In electron energy loss spectroscopy, one is interested in the inelastic energy losses suffered by the primary beam as a result of scattering. The energy changes may be due to the collective electron oscillations or inter-band transitions of the sample or the characteristic energy losses occurring due to core electron excitations resulting in characteristic edges superposed on a monotonically decaying background. While the former occur in the range of 5–50 eV, the other occurs within about a few thousand eV. The collective electron oscillations or inter-band transitions may not have much elemental or material significance as the energies of these transitions change with size at the nanometer level. At extremely low energies, these transitions may disappear altogether as well. The core electron excitations are characteristic of the element. Thus a qualitative analysis of the material is possible in terms of the characteristic energy losses obtained. An energy loss at 284 eV is characteristic of carbon and that at 530 eV is due to oxygen. The intensity at this energy loss after subtracting the background suitably is related to the concentration of the atom. Thus quantitative analysis is possible. The position and shape of the energy loss are characteristic of the chemical environment of the sample. Because of all these, electron energy loss spectroscopy at the nanometer scale is a unique probe.

We can calculate core level excitation spectra. In this, the approach will be to calculate the inelastic scattering cross section. The essential aspect of these computations will be to evaluate the probability of electronic transitions between two orbitals as a result of a perturbing electric field. Atomic orbitals of the initial states and molecular orbitals of the final states can be used for such computations. By performing refined calculations, it is possible to obtain a positive agreement between theory and the fine structures seen experimentally.

The energy loss information can be collected as a function of space. This can be done in two different modes, either as a spectrum image wherein at each point defined on the sample, one collects a complete spectrum or the spectrum in an energy window $\Delta E$ is collected for a two-dimensional space called 'image-spectrum'. Both the methods have their own advantages and disadvantages. The former is collected in the STEM and is superior in the sense that all spectral channels are collected parallely as a function of space. A post-column energy analyzer does the energy analysis of the electrons. In the image-spectrum mode, an energy filter is used. An imaging stage which converts the spectrum into an image is put after the

filter. The filter fixes the energy of the electrons to be transmitted and the slit at the exit plane of the filter decides the energy width.

EELS has been used for elemental mapping of materials at the nanometer range. Elemental mapping of doped elements in single-walled carbon nanotubes, nanobubbles in alloy matrices, segregation of atoms in ultra-thin films, etc. have been performed with EELS. Mapping of individual atoms in nanostructures has been demonstrated. Apart from elemental mapping, the distribution of the bonding characteristics of an element within a material at the nanometer level can be investigated. Measuring atomic properties of nanometer sized objects is a distinct reality with EELS.

## 2.2.7 *In-situ* Nano Measurements

Properties of individual nano objects have to be understood in a number of cases. This has a bearing on the properties of the bulk systems. For example, how would one measure Young's modulus of a single carbon nanotube? There are several methods one can use for this, but it is important to make the measurement with an instrument wherein the nano object is seen while the measurement is performed. There are several instances of this kind such as the measurement of electrical conductivity, thermal conductivity, temperature stability, melting point, chemical reactivity, etc. of single nano objects. All these are possible in the transmission electron microscope. Of course for each of these measurements, the TEM has to be modified significantly. It is also necessary to invent new methods and appropriate theory for the nano measurements.

One of the easier kinds of *in-situ* measurements in TEM (as well as in other cases) is temperature dependence. This measurement entails varying the sample temperature in the rage of liquid helium (or more generally liquid nitrogen) to 1200 K. The phase or morphology change of the material is investigated with specific reference to a single nano object. This kind of investigations reveal that different morphologies have different stability. For example, among a group of particles with cubic and tetrahedral shapes, the cubic one is found to change into a spherical structure at a lower temperature than the tetrahedral one. This is attributed to the lower surface energy of the [111] planes present in a tetrahedral structure than the [100] present on cubes.

One of the ways of measuring Young's modulus of a nanotube is to investigate the blurring contrast due to the thermal vibration of the tip of a carbon nanotube image. This is shown in Fig. 2.11. Some of the nanotubes, shown with arrows, show a blurring contrast. The blurring amplitude, $u$ can be related to the vibration energy, which is related to Young's modulus. By measuring the blurring contrast as a function of temperature, Young's modulus of a multi-walled carbon nanotube is calculated to be in the range of 1 TPa (Ref. 3).

Numerous different kinds of measurements have been demonstrated which include *in-situ* transport measurements in a nanotube, mapping the electrostatic potential at the tips, work function measurements of individual nano objects, field emission from nanotubes and applications of single nanotubes as balances. In several cases, it is necessary to develop new methods and appropriate theory. It is very clear that numerous kinds of nano measurements are possible in TEM with appropriate modifications of the equipment.

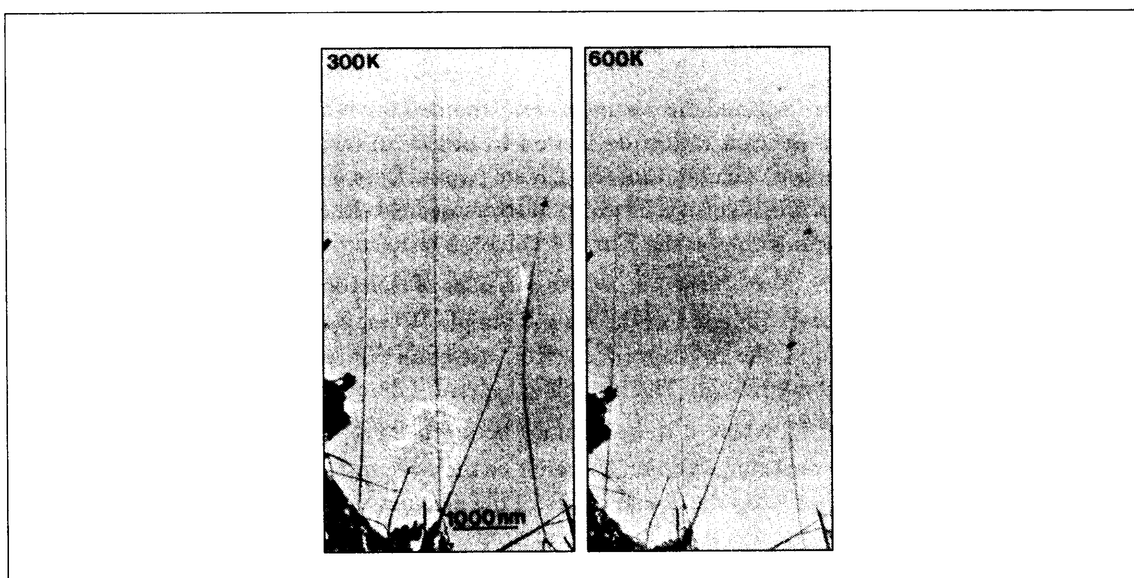



**Fig. 2.11**: *Low magnification TEM images of carbon nanotubes grown by the arc-discharge method. The tips of the nanotubes are blurred due to thermal vibrations. The amplitude of the vibrations increase with temperature. From Treacy, et al. 1996. Copyright Nature Publishing Group, used with permission from the author.*

## 2.3 Scanning Probe Microscopies

There are broadly two kinds of SPM techniques, namely scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Numerous variations of these techniques exist. The objective of this section is to review some of the most prominent of these techniques so as to give a flavour of them. Those interested in additional details may consult original papers and books, some of which are listed in the references.

In a scanning probe technique, a probe of nanometer dimensions is used to investigate a material. The investigation is conducted on the surface of the material. This is done by keeping the tip stationary and moving the sample or vice versa. The information that is collected by moving the sample can be of several kinds which differ from technique to technique. The collected data and its variation across the sample are used to create an image of the sample. The resolution of such an image depends on the sample, the control that one has on the movement on the tip/sample, and the inherent nature of the data.

## 2.3.1 Scanning Tunneling Microscopy

STM was developed (Ref. 4) in 1982 and the inventors were awarded the Nobel Prize for Physics in 1986. In STM, the phenomenon of electron tunneling is used to obtain an image of the topography of the surface. This utilizes the principle of vacuum tunneling. Here two surfaces, a tunneling probe and a surface are brought near contact, at a small bias voltage. If two conductors are held close together, their wavefunctions can overlap. The electron wavefunctions at the Femi level have a characteristic exponential inverse decay length, $K$ which can be given as, $K = \sqrt{(8m\varphi)/h}$, where $m$ is mass of electron, and $\varphi$ is the local tunneling barrier height or the average work function of the tip and sample. When a small bias voltage, $V$ is applied between the tip and the sample, the overlapped electron wavefunction permits quantum mechanical tunneling and a current, $I$ to flow through. The tunneling current, $I$ decays exponentially with a distance of separation as $I \alpha Ve^{-\sqrt{(8m\varphi)/h}2d}$, where $d$ is the distance between the tip and the sample and $\varphi$ is the work function of the tip. The tunneling current is a result of the overlap of electronic wave functions of the tip and the sample. By considering the actual values of the electron work functions of most materials (typically about 4 eV), we find that the tunneling current drops by an order of magnitude for every 1 Å of distance. The important aspect is that the tunneling current itself is very small and in addition, it is strongly distance-dependent. As a result, the direct measurement of vacuum tunneling was not observed till 1970s. Tunneling, however, was observed and was limited to tunneling through a barrier.

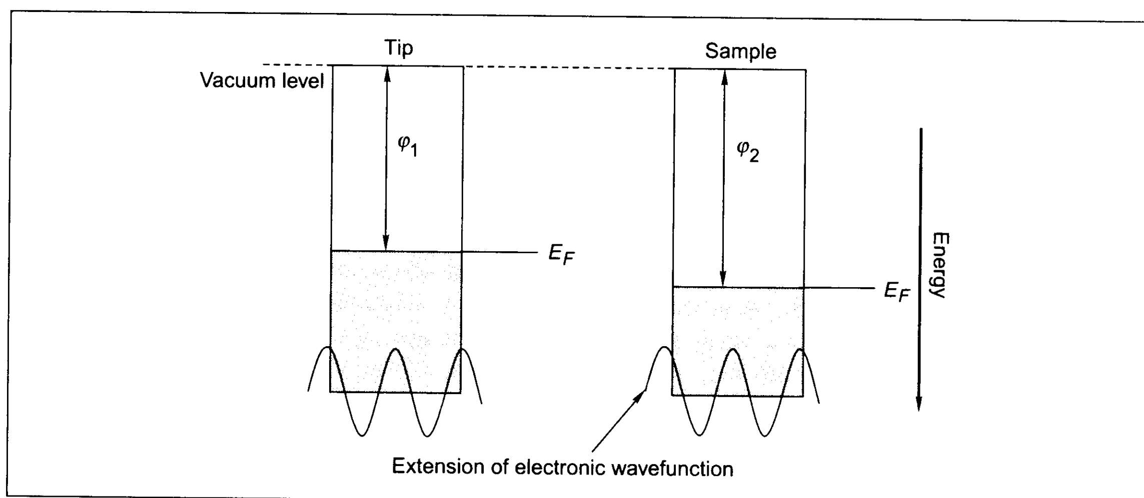



**Fig. 2.12:** *Electron energy states of the sample and the tip before the bias. When a sample and a tip are held close together there is a possibility of their electronic wave functions overlapping. $\varphi_1$ and $\varphi_2$ are the workfunctions of the tip and the sample, respectively.*

The basic principles of such a device are simple and are illustrated in Figures 2.12 and 2.13. In this, a tip is brought close to the sample so that the electrons can tunnel through the vacuum barrier. The position of the tip is adjusted by two piezoelectric scanners, with $x$ and $y$ control. The $z$-axis position is

continuously adjusted, taking feedback from the tunneling current so that a constant tunneling current is maintained. The position of the $z$-axis piezo therefore reproduces the surface of the material. The position of the piezo is directly related to the voltage supplied to the piezoelectric drives. Scanning is possible in the constant height mode as well, but this is done only on extremely flat surfaces so that the tip does not crash by accident. The other mode of imaging is by modulating the tip at some frequency and measuring the resulting current modulation. This helps in understanding the compositional variation across the sample.

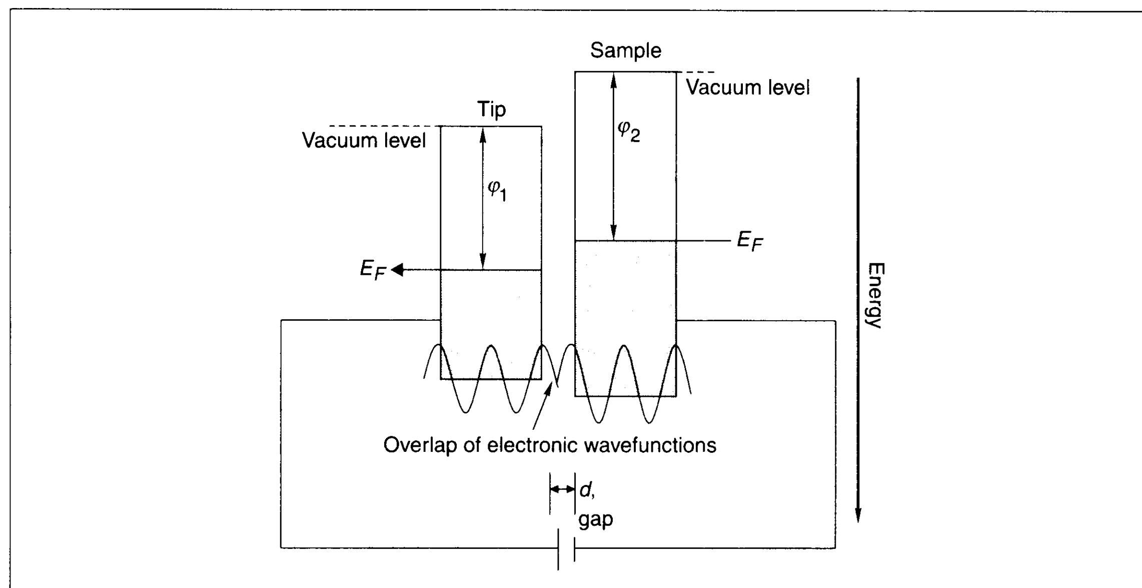



**Fig. 2.13:** *Electronic wavefunctions overlap at lower separations and a tunneling current is observed.*

Tunneling happens through a few atoms and it is believed that the STM images occur as a result of tunneling to a single atom or to a few atoms. The tip manufacturing process does not make one atomically sharp tip alone. However, what is apparently happening is that electron tunneling takes place to whichever atomically sharp tip which is closer to the surface.

STM has been used to understand numerous processes but a review of these is out of place here. Most of these studies relate to understanding various surface processes. The techniques available earlier for these studies before the arrival of STM, are low energy electron diffraction (LEED), reflected high energy electron diffraction (RHEED), X-ray diffraction and variations of these techniques. Instead of probing the average structure of the surface, as is possible with these techniques, STM allowed the investigation of local structures. These studies focused on surface reconstruction, adsorption, chemical transformations, etc. on metal, semiconductor and even on insulating surfaces (under appropriate conditions to observe tunneling current). In the brief discussion below, we shall illustrate a few of the experiments of relevance to nanoscience and technology.

STM provides information on the local density of states. The Density of States (DoS) represents the quantity of electrons existing at specific values of energy in a material. Keeping the distance between the sample and the tip constant, a measure of the current change with respect to the bias voltage can probe the local DoS (LDoS) of the sample. A plot of $dI/dV$ as a function of $V$ represents the LDoS. This is called scanning tunneling spectroscopy (STS). An average of the density of states mapped by using STM is comparable to the results from ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy (as discussed below). Such comparisons have been done in a few cases and the results indicate that the tip effects are unimportant. The important aspect is that such mapping of density of states is possible with spatial specificity.

Electrons can only tunnel to states which are present in the sample or tip. When the tip is negatively biased, electrons from the tip tunnel from the occupied states of the tip to the unoccupied states of the sample. If it is the other way, electrons tunnel from the occupied states of the sample to the unoccupied states of the tip. Thus a change in polarity makes it possible to probe the occupied or unoccupied states of the sample as illustrated in Fig. 2.14.

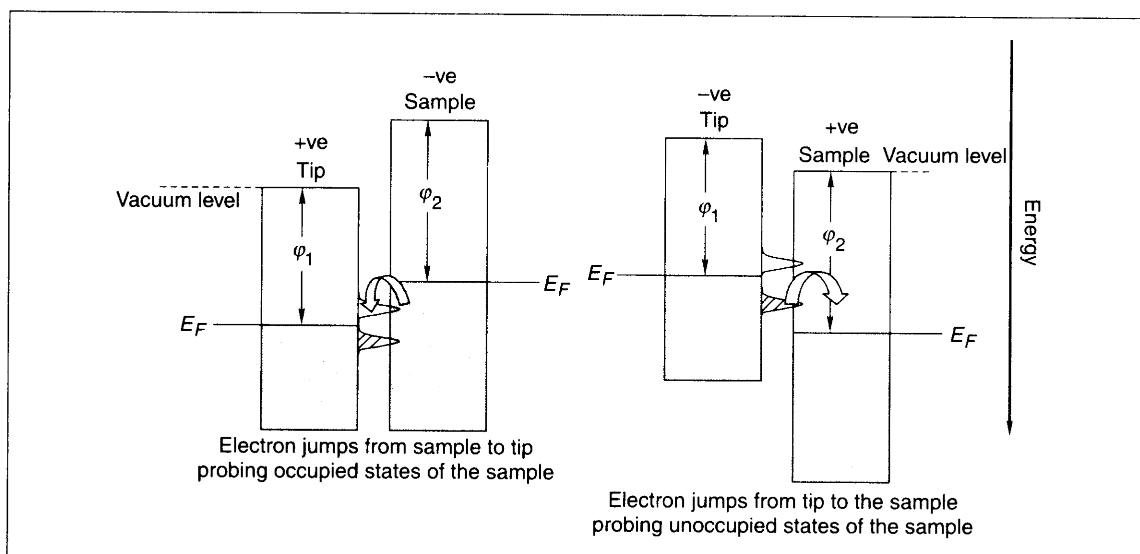



**Fig. 2.14:** *Depending on the sample bias, one can probe various kinds of states of the sample.*

STM has revolutionized a number of areas of fundamental science. Among the advantages of STM are its capability to analyze samples with atomic resolution, to see processes as they are occurring and to perform all these while the sample is in atmospheric conditions. In nanoscience and technology the uses of STM are manifold. An example is given here for the benefit of the reader. STM has been used in different ways to understand the electronic structure and properties of carbon nanotubes. An atomically resolved image (Ref. 5) of a single-walled carbon nanotube is shown in the Fig. 2.15. The arrangement of the hexagons is seen. One has to remember that the graphitic sheet has been folded so that the hexagons are not planar. From this, we can determine the tube axis and the chiral angle. The chiral angle is 7° for this

tube and the tube diameter is 1.3 nm. The STS measurements give the band gap and local electronic structure of the tubes.

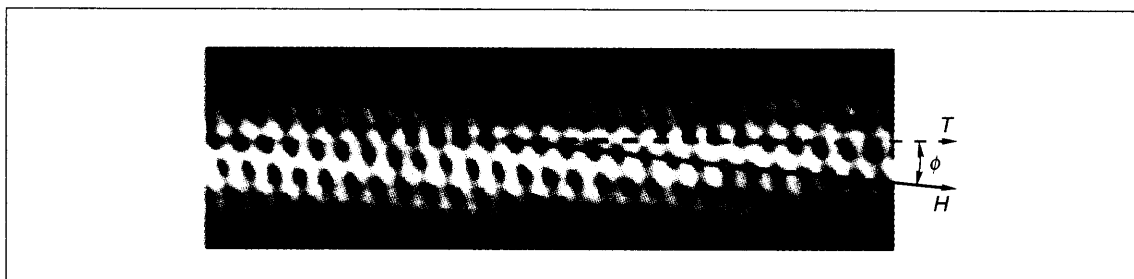



**Fig. 2.15:** *Atomically resolved STM images of an individual single-walled carbon nanotube. The lattice on the surface of the cylinders allows a clear identification of the tube chirality. Dashed arrow represents the tube axis T and the solid arrow indicates the direction of nearest-neighbour hexagon rows H. The tube has a chiral angle $\phi$ = 7° and a diameter d = 1.3 nm, which corresponds to the (11,7) type tube. See the chapter on carbon nanotubes. Check images, identification, corresponds. From Wildoer, et al., 1998 (Ref. 5). Copyright Nature Publishing Group.*

## 2.3.2 STM-based Atomic Manipulations

In a normal STM imaging process, the tip-sample interaction is kept small. This makes the analysis non-destructive. However, if the interaction is made big and as a result, the tip can move atoms on the substrate, there is a distinct possibility of writing atomic structures by using STM. This was done in 1990 by Eigler. When he manipulated Xe atoms on the surface of Ni(110) in a low temperature ultra high vacuum (UHV) STM instrument, a new branch of science was born (Ref. 6). The process of manipulating atoms is technically simple. This is schematically illustrated in Fig. 2.16. The STM scanning process is stopped and the tip is brought just above the sample atom. The tip is then lowered to increase the interaction between the tip and the atom. This is done by increasing the tunneling current (to the tune of ~30 nA). Note that the typical tunneling current used for imaging is of the order of 1 nA. As a result of this, the tip-atom interaction is strengthened and the tip can now be moved to the desired location. The interaction potential between the tip and the atom is strong to enable it to overcome the energy barrier so that the atom can slide on the surface. It is, however, not transferred to the tip from the substrate. After moving to the desired location, the tip is withdrawn by reducing the tunneling current. This process can be repeated to obtain the desired structure, atom by atom. A quantum corral built by arranging 48 Fe atoms on a Cu(111) surface (Ref. 7) is shown in Fig. 2.17 (Plate 2). The electron waves confined in the corral are seen in this picture. The confinement of electrons comes about as a result of the nano structure constructed. At such length scales, quantum mechanical phenomena can be observed. By having an elliptical corral of Co atoms and placing another Co atom at one of its foci, the other focus manifests some of the features of the atom, wherein no atom exists. When the atom is moved from the focus, the effect disappears (Ref. 8). This quantum mirage effect suggests the transportation of data in the quantum mechanical size limit.

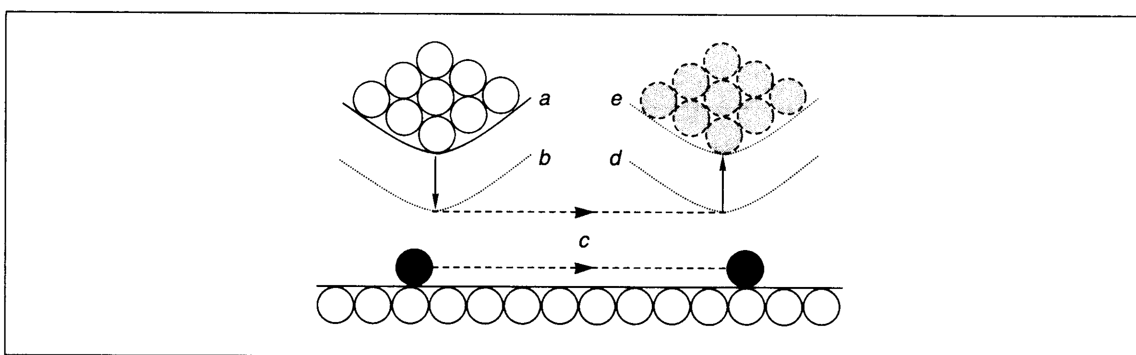



**Fig. 2.16:** *Process of manipulating atoms on the surface. An STM tip at position **a** is brought to position **b** by vertical movement at which point the tunneling current is large. Then the tip is slid over the surface to the desired location **d**, and subsequently the tip is brought back to position **e**.*

Numerous other manipulation strategies have been demonstrated. Tunneling current has been used to break chemical bonds. This has been shown in the case of oxygen and organic molecules. In the case of organic molecules, the detached fragments have been moved and further recombined in the desired fashion. Feynman's prediction of atomically constructed matter has come true.

Numerous modifications of STM are available. A list of variants is reproduced in Ref. 9 in the Reference list. The reader may consult the references and additional reading material listed at the end of the chapter. The most current developments are in the areas of fast scanning STM, ultra low temperature STM and spin polarized STM. In the first, the dynamic processes taking place at the surface such as a chemical reaction are monitored and the images are captured so as to construct a movie. This can be combined with a solution phase STM so that the reactions in solutions can be investigated. In spin polarized STM, a magnetic tip is used so that the tunneling current is sensitive to the spin. In ultra low temperature STM, the measurements are done at the milliKelvin temperature range so that the phenomena at low temperatures can be probed.

## 2.3.3 Atomic Force Microscopy

In this technique, the interactions between a sharp probe and a sample are used for imaging. The cantilever which probes the surface has an atomically sharp tip which is brought into contact with the surface. The large scale use of AFM today is because of the application of microfabricated tips of Si or $Si_3N_4$. The spring constant of the tip is of the order of 1 N/m and the shortest vertical displacement, $d$ measurable can be obtained from, $<1/2\ kd^2> \sim \frac{1}{2}\ k_BT$. With $k_BT$ of the order of $4 \times 10^{-21}$ J at 298 K, the smallest vertical displacement observable is 0.5 nm. The extent of interaction between the cantilever and the tip is measured by cantilever displacements. The interaction between the tip and the sample is of the order of a nano Newton, which is not directly measured in AFM. The displacement of the cantilever is monitored by the reflection of a laser from the back of the cantilever, detected on a segmented photodetector. A four-segment photodiode is used for this purpose. In the very first AFM, the interaction was measured by the

difference in tunneling current, with the tip being fixed on the back of the cantilever. This allows the detection of normal and lateral displacements of the cantilever. Optical detection is far superior to other forms of detection, though there are problems associated with the laser such as the heating of the cantilever and the sample. The image is generated from the interaction force. In the scan, the interaction force is kept constant by a feedback control. The increase in the interaction force when the tip approaches an elevated part is related to the vertical displacement of the scanner needed to eliminate this increase in signal. This is converted to height. Thus the basic components of the microscope are the cantilever, the detection system, scanners and the electronics. These components are schematically represented in Fig. 2.18. This also suggests that depending on the kind of interactions between the cantilever and the surface, various kinds of microscopies are possible. The probe can be made magnetic to investigate the magnetic interactions with materials. This results in magnetic force microscopy. The tip can have specific temperature probes or the tip itself can be made of a thermocouple. This facilitates scanning thermal microscopy (SThM). The tip may be attached with molecules which are designed to have specific molecular interactions with the surface. This results in chemical force microscopy. There are several such variations, some of which are listed under Ref. 9.

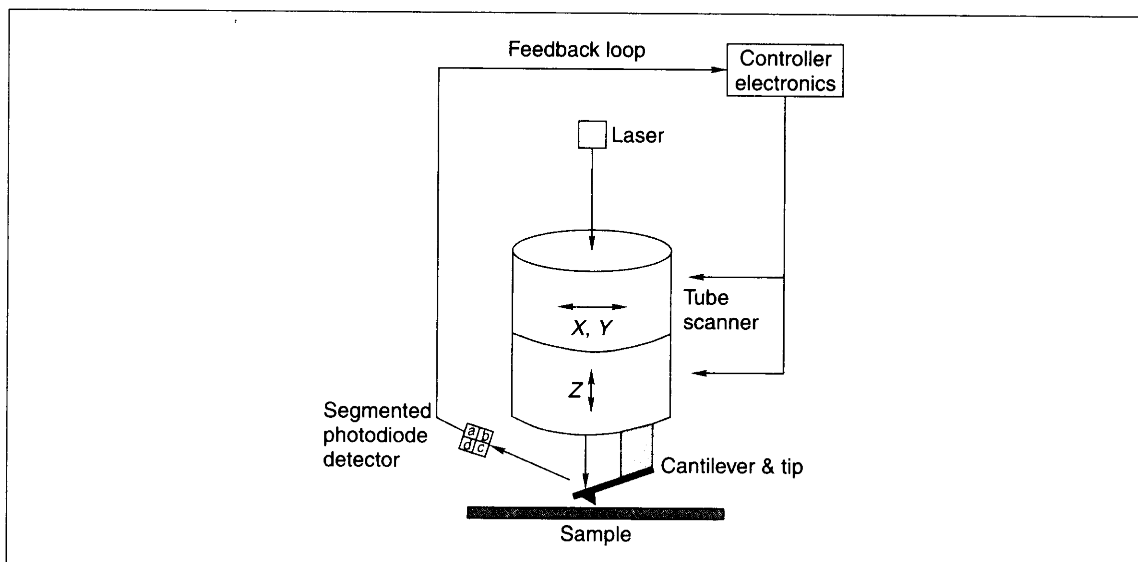



**Fig. 2.18**: *Schematic representation of an atomic force microscope. The sample surface is scanned by the cantilever, connected to a tubular scanner. The principal functional units in it are three piezoelectric scanners. The deflections of the cantilever are monitored by the segmented photodiode detector.*

Resolution in scanning probe microscopy cannot be defined in the same way as for optical methods, wherein the diffraction limit determines the resolution that is practically achievable. SPM is a three-dimensional imaging technique and the resolution is affected by the tip geometry. As would be seen in Fig. 2.19, improved resolution can be obtained for sharper tips. In practical description of resolution, especially in the biological context, the width of DNA measured is considered as a measure of resolution.

DNA in its $\beta$ form is known to have a diameter of 2 nm. Width alone is not enough to describe the resolution as SPM is a three-dimensional technique and height is important.

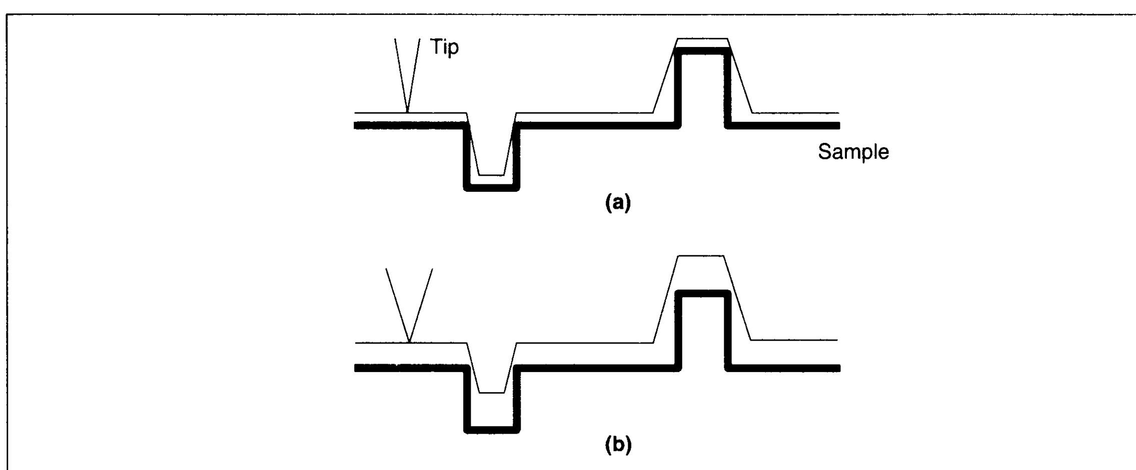
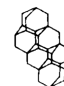



**Fig. 2.19:** *Resolution in SPM depends on the tip details; (a) gives better resolution in comparison to (b).*

AFM is commonly operated in two modes, the contact mode and the non-contact or tapping or intermittent contact mode. In the contact mode, the tip comes into contact with the surface. The force between the sample and the tip is the product of the displacement of the tip and the force constant of the cantilever ($f = -kx$). The contact with the surface allows an evaluation of the surface friction. When the interaction is strong, the surface damage can be significant, which makes the contact mode difficult to use for soft materials.

In the non-contact mode of operation, the tip is oscillated at its resonant frequency by an actuator. The decrease in the amplitude of the motion when the cantilever comes close to the sample is used to measure the tip-sample interaction. The drop in the amplitude is set to a pre-determined value. The intermittent contact that the tip makes is gentle and does not damage the material, though the probes are generally harder. Since it is a gentle mode of scanning, the non-contact mode is the most often used, especially in the case of materials with surfaces delicate such as a polished silicon wafer.

Typical AFM images have a resolution of the order of 5 nm. Atomic features have been observed, but this is not a routine development. In the case of specially fabricated tips, a resolution of 1 nm can be observed. True atomic features have been demonstrated in specific cases. The best known examples of nanoscale structures are DNA strands. Images of DNA spread on mica are shown in Fig. 2.20 (Ref. 10). These images show variations in the shape and width of the curved structures depending on the type of imaging. The width of the molecule seen in AFM images need not be of the actual width due to several factors. One of the factors is that it corresponds to the relaxation of the molecule on the substrate on which it is held for imaging. The other factors has to do with the tip-induced deformation in the sample. On the contrary, the contour length of the macromolecule is a measure of the molecular weight of the material.



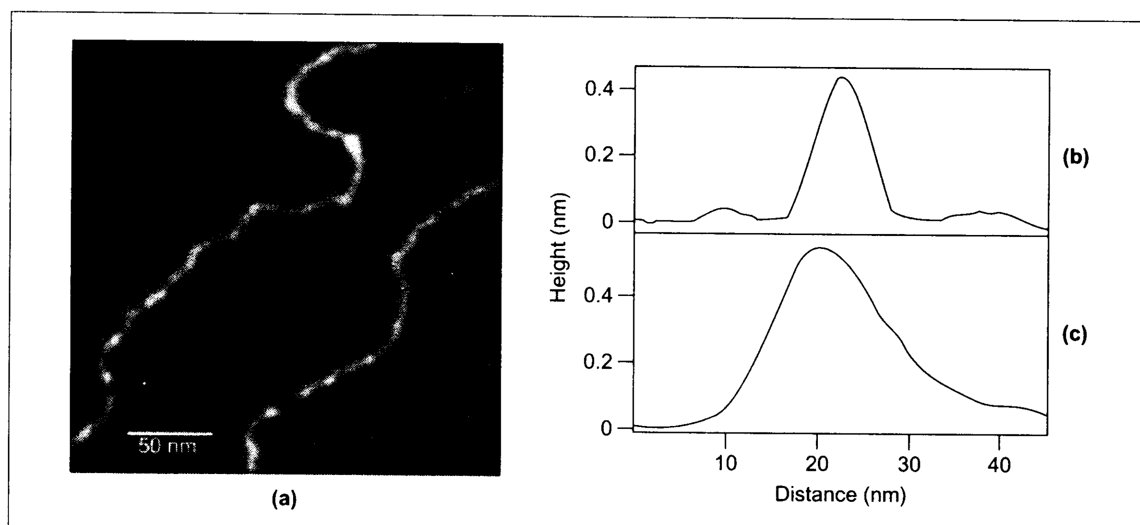



**Fig. 2.20:** *(a) Height image obtained with a SWNT tip of double-stranded DNA adsorbed on mica. (b) Typical height cross section from the image in (a). The FWHM is 5.6 nm. (c) Typical height cross section from an image of the lambda-DNA obtained with a conventional Si tip. The FWHM is 14.4 nm. Reused with permission from Wong et al. (Ref. 10). Copyright 1998, American Institute of Physics.*

Mechanical properties are measured by using AFM. It is important to correlate these properties to the chemical composition and structure in order to facilitate a complete understanding of the material. This can be done by combining spectroscopy with imaging. Although a few such tools such as confocal Raman microscopy and infrared microscopy are available, the spatial resolution is of the order of microns or hundreds of nanometers. A combination of AFM with spectroscopy will be immensely useful. Scanning near-field optical microscopy with Raman microscopy could prove to be useful in this regard, but the current resolution of this is only of the order of 50 nm.

## 2.3.4 Scanning Probe Lithography (SPL)

Manipulating objects and the tools associated with such manipulation are the central aspects of the development of civilizations. The names of various civilizations are coined on the basis of the tools used, such as the Stone Age, Iron Age, etc. In each of these ages, different kinds of tools were used to manipulate objects, which were mostly of large or macroscopic dimension. In the nano era, atoms are manipulated.

SPL refers to the use of SPM-based techniques for modifying substrates by the application of various actions such as scratching, writing, chemistry, photo-irradiation, etc. in a spatially confined manner. The structures that one can make as a result of these manipulations are of the order of 10–100 nm. These techniques are summarized in Table 2.4 (Ref. 11).

There are basically three kinds of probes with which SPL can be done. These are STM, AFM and SNOM, each of which is discussed separately elsewhere in this book. The motivation to use these

**Table 2.4**: *Scanning Probe Lithographic Techniques. Adapted from S. Hong, et al., 2005 (Ref. 11).*

| | SPL Method | Instruments | Environment | Key Mechanism | Typical Resolution | Patterning Materials | Possible Applications |
|---|---|---|---|---|---|---|---|
| Nanoscale Pen Writing | Dip-Pen Nano-lithography | AFM | Ambient | Thermal Diffusion of Soft Solid | ~10 | SAM, Biomolecules Sol-Gel, Metal, etc. | Biochip, Nanodevice, Mask Repair, etc. |
| | Nanoscale Printing of Liquid Ink | NSOM | Ambient | Liquid Flow | ~100 nm | Etching Solution, Liquid | Mask Repair, etc. |
| Nanoscale Scratching | Nanoscale Indentation | AFM | Ambient | Mechanical Force | ~10 nm | Solid | Mask Repair, etc. |
| | Nanografting | AFM | Liquid Cell | Mechanical Force | ~10 nm | SAM | Biochip, etc. |
| | Nanoscale Melting | AFM | Ambient | Mechanical Force and Heat | ~10 nm | Low Melting Point Materials | Memory, etc. |
| Nanoscale Manipulation | Atomic and Molecular Manipulation | STM | Ultrahigh Vacuum (Often Low Temperature) | van der Waals or Electrostatic Forces | ~0.1 nm | Metals, Organic Molecules, etc. | Molecular Electronics, etc. |
| | Manipulation of Nano-structures | AFM | Ambient | van der Waals or Electrostatic Forces | ~10 nm | Nanostructure, Biomolecules, etc. | Mask Repair, Nanodevices, etc. |
| | Nanoscale Tweezers | Possibly AFM | Ambient | van der Waals or Mechanical Forces | ~100 nm | Nanostructures | Electrical Measurement, etc. |

*Contd...*

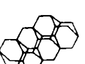




*Table 2.4 Contd...*

| | SPL Method | Instruments | Environment | Key Mechanism | Typical Resolution | Patterning Materials | Possible Applications |
|---|---|---|---|---|---|---|---|
| Nanoscale Chemistry | Nanoscale Oxidation | STM or AFM | Humid Air | Electro-chemical Reaction in a Water Meniscus | ~10 nm | Si, Ti, etc. | Nanodevices, etc. |
| | Nanoscale Desorption of SAM | STM or AFM | Humid Air | Electro-chemical Reaction in a Water Meniscus | ~10 nm | SAM | Nanodevices, etc. |
| | Nanoscale Chemical Vapour Deposition | STM | Ultrahigh Vacuum with Precursor Gas | Nanoscale Chemical Vapor Deposition | ~10 nm | Fe, W, etc. | Magnetic Array, etc. |
| Nanoscale Light Exposure | Nanoscale Light Exposure | NSOM | Ambient | Photoreaction | ~100 nm | Photosensitive Materials | Nanodevices, etc. |

lithographic techniques is to overcome the limit of current technology. The semiconductor industry is dependent on ultraviolet lithography, which uses ultraviolet rays to pattern surfaces, which are pre-coated with a photoresist. The chemical reactions on the resist will eventually strengthen or weaken the molecular bonding in the resist and a pattern can be made by subjecting the modified resist-coated material to a solvent wash. The pattern thus created can be used in an etching process. The process can be repeated and a complicated structure can be created on the surface. This process can be undertaken on large sizes of device structures and a huge number of devices can be made on small areas, which is the basis of semiconductor technology. The smallest structures that can be created today are of the order of ~90 nm, using ultraviolet light of ~190 nm wavelength. The lithography technique meets its natural limits as the size approaches the resolution limit of the optical techniques. This is given by the Rayleigh equation, resolution = $k\lambda/NA$ where $k$ is a constant and $NA$ is the numerical aperture of the lens system ($n \sin\theta$, where $\theta$ is the angle of incidence and $n$ is the refractive index of the medium). The resolution is normally taken to be approximately $\lambda/2$. As a result, reduction in the size of structures possible using X-ray lithography, e-beam lithography and stamping-based methods is being investigated.

Although SPL methods are important tools, they are serial techniques as the probe makes the transformation in steps. In this they have a distinct disadvantage in comparison to the traditional methods. However, it is important to note that the transformations carried out by lithographic methods generally involve higher temperatures of the order of 100 °C and at such temperatures, biological materials lose activity. SPL does not require higher temperature and the methods used are generally delicate. This allows the use of such techniques for manipulating biological or soft materials. With the bio-nano interface growing significantly, SPL-based lithography is bound to find newer applications.

## 2.4 Optical Microscopies for Nanoscience and Technology

The minimum distance that an optical microscope can resolve is: $\Delta x = 0.61\ \lambda/n\sin\theta$, where $\lambda$ is the wavelength of the light in vacuum, $\theta$ is the collection angle and $n$ is the index of diffraction. One can improve the resolution by decreasing the wavelength of illumination, by decreasing $n$ or by increasing $\theta$. However, irrespective of the various improvements, the fundamental limits imposed by the methodology cannot be overcome. When it comes to particle beams such as electrons, the image resolution can be increased as electrons at high energies have very short wavelengths.

Light, especially visible light, enjoys a lot of advantages in the investigation of matter in spite of its limitations. One advantage is that light at this energy does not modify matter as the energy involved is small. Light also results in excitations in matter which leads to phenomena such as fluorescence, that can be used for studying materials with chemical specificity. Light also leads to absorption and inelastic scattering, both of which can be used for imaging purposes. These are also molecule-specific.

Improved resolution in optical microscopies can broadly be brought about in two different ways. The first belongs to far field imaging and the second to near field imaging. In the former, the illumination occurs at a distance several microns away from the object to be imaged and in the latter, it occurs within distance of a few nanometers from the surface. While the former looks at the bulk features of the sample,