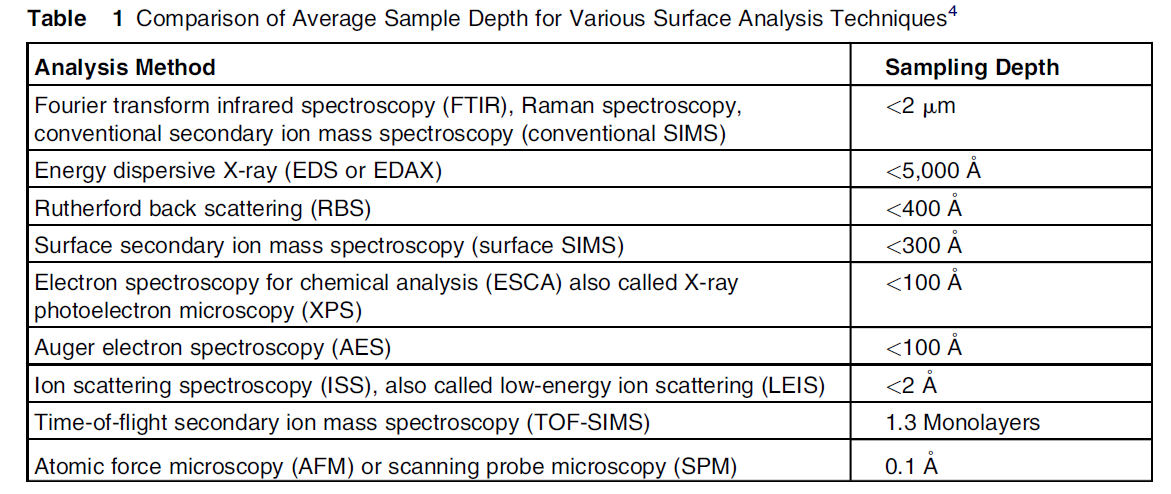
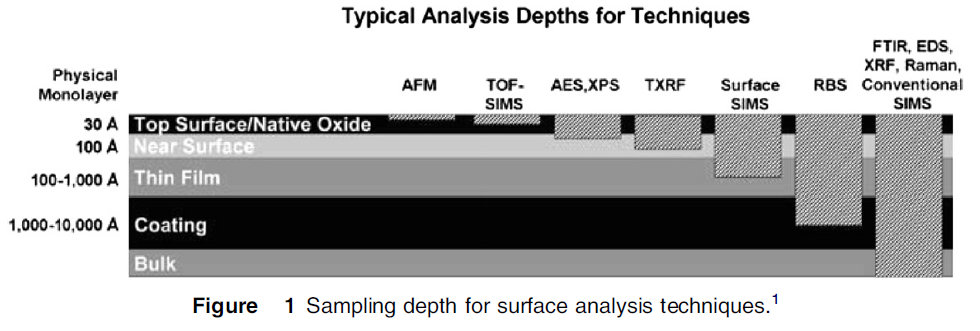
**Surface Characterization Techniques**

**Introduction**

In the analysis of adhesion bonding, possessingknowledge of the composition and structure of the adhered surface is important. Characterization of bonding surfaces aids both in design and failure analysis of a bond, should the adhesion bond fail.

Surface analysis is the use of microscopic chemical and physical probes that give information about the surface region of a sample. The probed region may be the extreme top layer of atoms (the only true surface, for purists), or it may extend up to several microns (millionths of a meter) beneath the sample surface, depending on the technique used. Analysis provides information pertaining to chemical composition, level of trace impurities, and physical structure or appearance of the sampled region. Such information is important to researchers and manufacturers who must understand the materials in order to verify a theory or to create a better product.



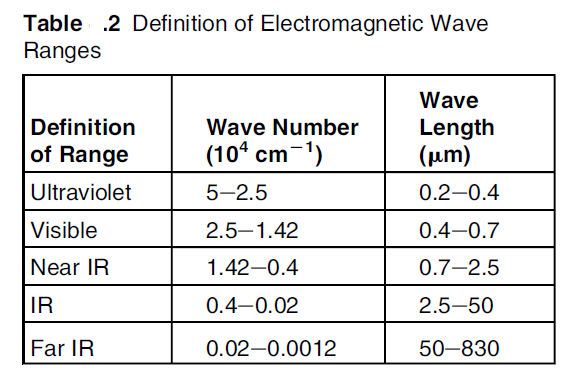


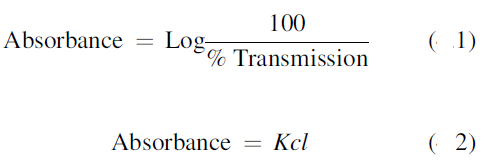
**Infrared Spectroscopy**

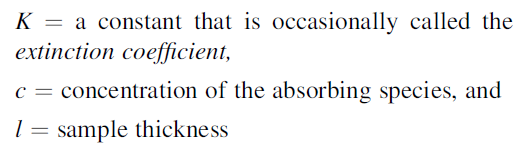
Infrared spectroscopy (IR spectroscopy or vibrational spectroscopy) involves the interaction of [infrared](https://en.wikipedia.org/wiki/Infrared) radiation with [matter](https://en.wikipedia.org/wiki/Matter). It covers a range of techniques, mostly based on [absorption spectroscopy](https://en.wikipedia.org/wiki/Absorption_spectroscopy). As with all spectroscopic techniques, it can be used to identify and study [chemicals](https://en.wikipedia.org/wiki/Chemical).

Samples may be solid, liquid, or gas. The method or technique of infrared spectroscopy is conducted with an instrument called an infrared spectrometer (or spectrophotometer) to produce an infrared spectrum. An IR spectrum can be visualized in a graph of infrared light [absorbance](https://en.wikipedia.org/wiki/Absorbance) (or [transmittance](https://en.wikipedia.org/wiki/Transmittance)) on the vertical axis vs. frequency or wavelength on the horizontal axis. Typical [units](https://en.wikipedia.org/wiki/Units_of_measurement) of frequency used in IR spectra are [reciprocal centimeters](https://en.wikipedia.org/wiki/Reciprocal_centimeters) (sometimes called [wave numbers](https://en.wikipedia.org/wiki/Wave_number)), with the symbol cm−1. Units of IR wavelength are commonly given in [micrometers](https://en.wikipedia.org/wiki/Micrometre) (formerly called "microns"), symbol μm, which are related to wave numbers in a [reciprocal](https://en.wikipedia.org/wiki/Multiplicative_inverse) way. A common laboratory instrument that uses this technique is a [Fourier transform infrared](https://en.wikipedia.org/wiki/Fourier_transform_infrared_spectroscopy) (FTIR) [spectrometer](https://en.wikipedia.org/wiki/Spectrometer).

[Fourier transform](https://en.wikipedia.org/wiki/Fourier_transform) infrared (FTIR) spectroscopy is a measurement technique that allows one to record infrared spectra. Infrared light is guided through an [interferometer](https://en.wikipedia.org/wiki/Interferometer) and then through the sample (or vice versa). A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal directly recorded, called an "interferogram", represents light output as a function of mirror position. A data-processing technique called [Fourier transform](https://en.wikipedia.org/wiki/Fourier_transform) turns this raw data into the desired result (the sample's spectrum): Light output as a function of infrared [wavelength](https://en.wikipedia.org/wiki/Wavelength) (or equivalently, [wavenumber](https://en.wikipedia.org/wiki/Wavenumber)). As described above, the sample's spectrum is always compared to a reference





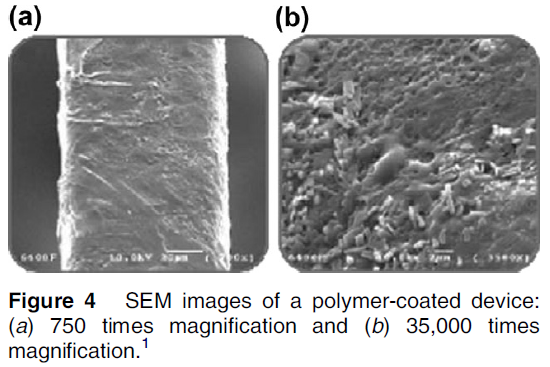


Equation (2) can be used to determine the concentration of a compound in a solution, if the value of K is known for that compound. Chemical bonds such as C-O, O-H, and so on, absorb different amounts of infrared energy over various wavelengths. Absorption patterns vary from sharp to broad for different bonds. Peak IR absorption wavelength (wave number) is characteristic of a chemical bond. Absorption over the infrared spectrum is a fingerprint characteristic of an organic material. Qualitative identification can be achieved by obtaining and analyzing the IR spectrum of a material.

**Scanning Electron Microscopy (SEM)**

SEM is a useful technique for the analysis of plastics surfaces. Actually, it is useful for any surface that survives in a vacuum. Almost all SEMs start by sputtering the surface with a thin layer of gold metal. If it is not already conductive, this makes the surface conductive, which is a requirement; so, you are often not looking directly at the surface. It involves a finely collimated beam of electrons that sweeps across the surface of the analysis specimen. The beam is focused into a small probe that scans across the surface of a specimen. The beam interactions with the material result in the emission of electrons and photons as the electrons penetrate the surface. The emitted particles are collected with the appropriate detector to yield information about the surface. The final product of the electron beam collision with the surface topology of the sample is an image (Fig. 4).

For example, Fig. 4 shows the result of topical SEM analysis of a drug-infused polymer coating on a stainless steel device. SEM of the surface at 750 times magnification is shown in Fig. 4. (a) and at 35,000 times magnification in Fig. 4. (b).



The higher magnification revealed the presence of crystals on the surface of the coating. A helpful attachment to the SEM is the electron microprobe. An electron beam is focused on a sample surface, causing ionization to a depth of a few micrometers. Energies and wavelength of the emitted X-ray during the de-excitation cycle are characteristic of the elements present in the top layers of the sample. The result is not a true surface analysis, but the electron microprobe allows analysis of various spots of the sample surface.

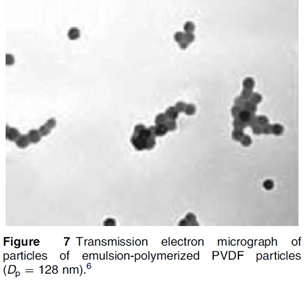
**Transmission Electron Microscopy (TEM)**

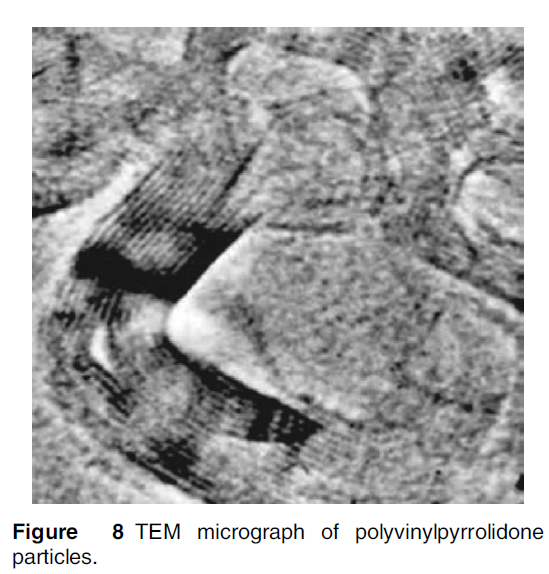
Transmission electron microscopy is similar to SEM, except for the fact that the beam passes through the sample. A high voltage (80-200 keV), highly focused electron beam is passed through a thin solid sample, typically 100-200 nm in thickness. Electrons undergo coherent scattering or diffraction from lattice planes in the crystalline phase of materials, thus yielding phase identification.

Characteristic X-rays that are generated can be detected in a separate detector, permitting qualitative elemental analysis. Figure 7 shows a TEM micrograph of particles of polyvinylidene fluoride that have been producedby emulsion-polymerization in an aqueous phase.

Figure 8 shows the capability of TEM in revealing the structure of a material. The authors have used nonaqueous miniemulsions to perform polymerizations.

Polyvinylpyrrolidone nanoparticles (Fig. 8) can be synthesized at temperatures higher than 150 ºC in nonaqueous inverse miniemulsions and in the presence of an additional stabilizer.

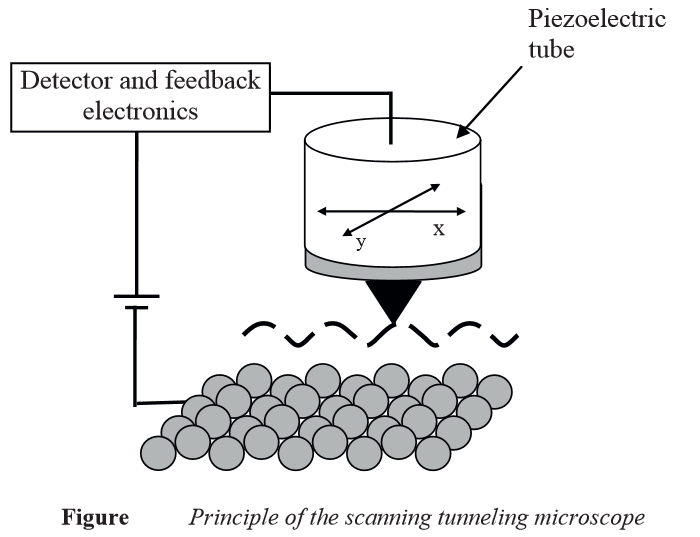




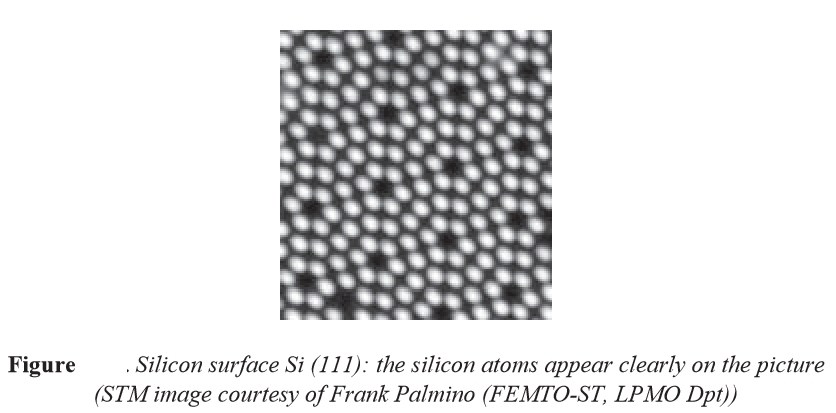
Particle size and size distribution can be measured from the micrograph because of its excellent resolution.

**Scanning tunneling microscope (STM)**

STMs (see Figure below) enable the study of topography and the local properties of metallic and semi-conductor surfaces with angström-level resolution [STI 04]. The principle of operation of the STM is based on measuring the electric current that arises due to the tunneling effect between a fine probe and the sample surface when these are separated by a few angströms (0.3–1 nm), and subject to a potential difference of a few tens of millivolts (10 mV to 1 V). The probes used are generally made of tungsten or of platinum-iridium and have radii of curvature of a few nanometers.



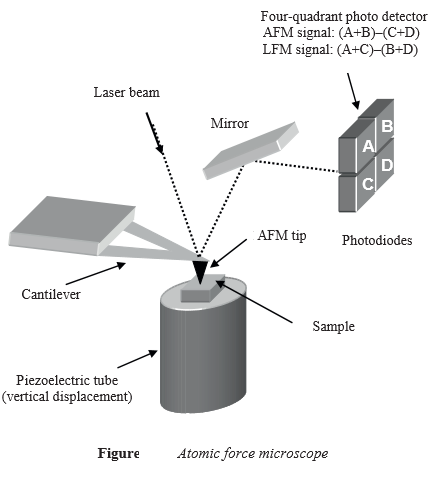
As the probe scans the surface, an electronic control system measures the tunneling current and moves the probe tip away from or towards the surface to ensure a constant current intensity. By recording the variations of the distance between the probe and the surface as a function of the coordinates of the scanned points, an atomic-scale 3D representation of the topographic surface is obtained (Figure below).



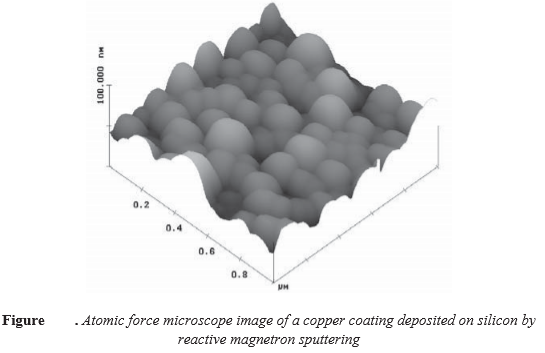
**Atomic force microscope (AFM)**

One of the main limitations of the STM is that it cannot be used to analyze nonconducting materials. To overcome this, other techniques such as the atomic force microscope (AFM) have been developed.

This microscope is sensitive to forces resulting from the interactions (see section 2.5.1) between the surface and a fine probe fixed to the tip of a coil spring plate or cantilever with a low spring constant (0.1–10 N m–1). When subjected to these forces (with intensity ranges of 10–13–10–6 N) the cantilever is subject to a deflection of a few tens of nanometers which is recorded by measuring the variation of the laser beam position reflected by the extremity of the cantilever (see Figure).

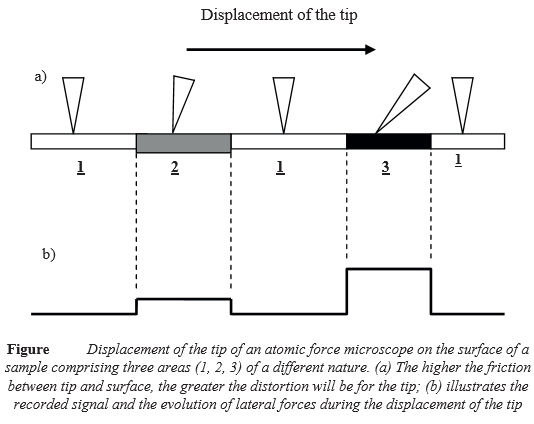


The 3D image of the surface can therefore be reconstructed after computer analysis of the recorded deflections as a function of the coordinates of the points examined (see Figure below). The probes used are usually made of silicon nitride (Si3N4) and have radii of curvature ranging from a few nanometers to a few tens of nanometers. Atomic-scale resolution can also be achieved with this type of microscope, using an ultrafine probe with a single atom at its tip.



When in contact mode, the tip of the atomic force microscope remains in contact with the surface and scans its topography. The drawback of this method for soft materials, however, is that it can scratch or deform the sample surface. In such cases, we use the AFM in vibration mode where the probe is maintained a few nanometers from the sample surface and subject to vibratory movement.

In contact mode, it is also possible to measure friction between the probe and the sample. This is referred to as the friction mode and the device used is called a lateral force microscope. As a result of frictional forces, the cantilever is subject to distortions which modify the trajectory of the reflected laser beam (see Figure).



The use of a four-quadrant photodetector allows the simultaneous detection of the vertical and lateral deviations of the light beam: the former defining the topographic state of the surface and the latter allowing friction measurements Atomic force microscopes can also detect and map the electrostatic and magnetic forces at the surface of a sample. In order to do this, the AFM is used in vibration mode with the probe placed about 0.5 micron from the surface (far field vibration mode). At that distance, only electric and magnetic forces can be detected. Other forces, such as the Van der Waals, chemical bonds or capillary forces (see section 2.5.1) are only detectable at closer distances (a few tens of nanometers).

**Stylus profilometers**

Stylus profilometers (or 3D profilometers) are devices equipped with a mechanical stylus consisting of a diamond tip whose radius of curvature is generally between 1 and 2 μm. The surface to be analyzed is moved under the stylus by two stepping motors that allow orthogonal movements with micron-level steps. The vertical movements of the stylus follow the topographic defects of the surface and are analyzed using a sensor that generates an electrical signal which is in turn digitized and processed by computer (see Figure).

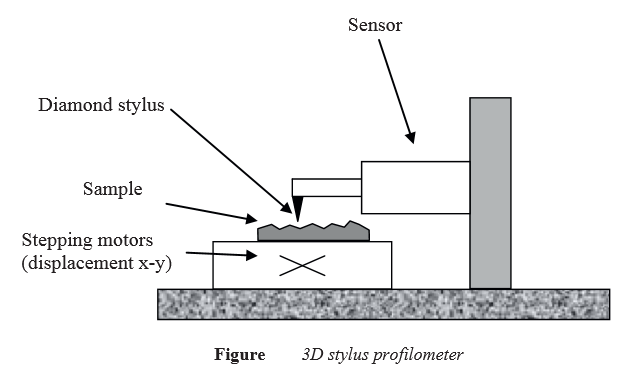
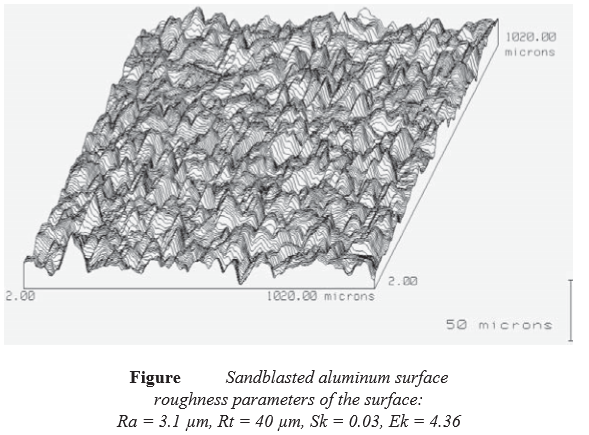


Figure shows an example of 3D topographic measurement of a surface.

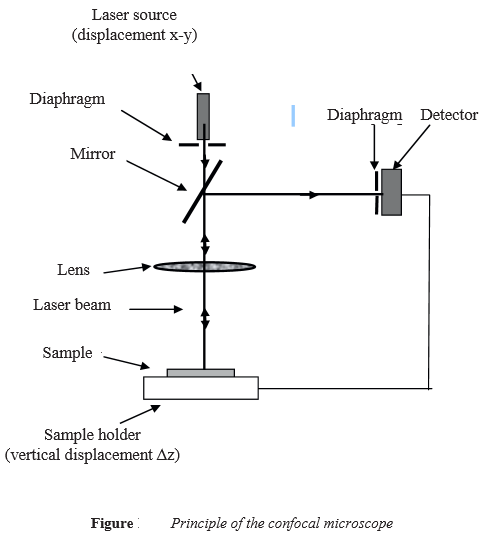


**Optical systems**

Measuring the state of a surface through optical (non-contact) methods uses a laser beam or white light beam to scan the sample surface. In certain cases, it is possible to use “full field” methods employing cameras to avoid the need for scanning.

**The confocal microscope**

The principle of the laser scanning confocal microscope is shown in Figure.



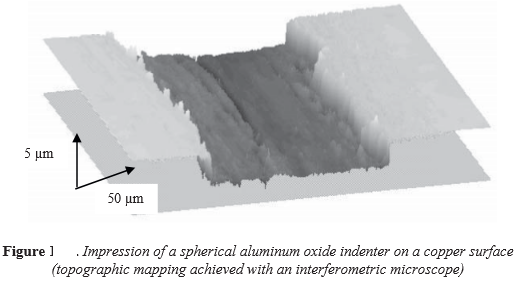
Small diaphragms (of a few microns in diameter) are placed in front of the laser source and just before the detector, allowing the size of the light source to be reduced to a point. The two diaphragms are placed in conjugate focal planes such that a single lens can focus both incident and reflected beams.

The laser scans the sample surface point-by-point along a line with a step x, repeated along parallel lines separated by a step y. The beam is reflected from the surface and then focused on the detector. This allows data collection of the 2D topography of the surface xy at a given height z as determined by the focal plane of the laser beam. The height of the sample is then moved by a step ∆z and a new phase of data collection is carried out. The 3D representation of the surface is obtained through the combination of the data extracted from the different images obtained at different heights z, with vertical and lateral resolutions of the order of 200 nm.

**The interferometric microscope**

The interferometric microscope consists of an optical microscope coupled to a two-beam optical interferometer of the Michelson, Mirau or Linnik type. In practice, an optical microscope can be converted to an interferometric microscope by replacing the standard objective with an interferometric objective, and by the addition of a high-resolution vertical translation stage.

The device operates as follows: a CDD camera records and digitizes a series of interferograms formed by the combination of a reference beam (reflected from the internal mirror of the interferometric objective) and the beam reflected from the surface of the sample. The interferograms recorded at different heights are processed by specialized software able to reconstruct the surface topography (see Figure).



**Local probe microscopes**

Local probe microscopes (or near-field microscopes) are very high resolution instruments for surface characterization that exhibit dramatically improved performance compared with stylus or optically based profilometry. Local probe microscopes exploit very short-range interactions between a fine probe and the sample surface to yield ultra-high resolution, ranging from a micron to a fraction of a nanometer. They systematically use a scanning technique, with the image obtained resulting from the complete scanning of the surface, which can lead to relatively long acquisition times. The resolution of these images essentially depends on two factors: the size of the probe and the way in which the probe–surface interaction varies as a function of the distance to the surface.