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ORIGINAL CONTRIBUTION

Atomic force microscopy, a tool for characterization, synthesis and chemical processes

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Abstract Atomic force microscopy (AFM) has become not only a topographic characterization tool of surfaces at a micro- or nano-level resolution but also a full line of research. From a topographic analysis of a surface to nanolithography or synthesis of particles, the AFM is used on a wide range of applications in physics, materials science, chemistry, and biology. This contribution presents a review of the uses of the instrument and the basic principles and techniques that are available in both static modes and dynamic modes. It focuses on the description of the main physical properties that can be obtained with the AFM and the experimental results of the instrument in materials science, chemistry, and biology.

Keywords Atomic force microscopy · Scanning force microscopy · Scanning probe microscopy · Contact mode · Non-contact mode · Tapping mode · Physical properties · Electrical properties · Mechanical properties · Magnetic properties · Chemical force microscopy · Force Spectroscopy · Piezoelectricity · Electrostriction · Magnetostriction

Introduction

Since its birth in 1986, atomic force microscopy (AFM) has become a very important characterization technique [1]. The number of publications using the different versions of scanning probe microscopy in which AFM is included is about 33,933 compared to scanning electron microscopy, which is about 56,695, a well-established characterization technique [2]. This numbers offer an idea on how important AFM has become.

In AFM, a tip connected to a cantilever interacts with a surface. The interaction could be by Van der Waals, electrical, magnetic, short range, capillarity, or any other electromagnetic force. This special mixture of variety of interactions gives AFM the possibility to be used not only to image surfaces, although most of its applications are done with that objective, but also to measure physical properties and participate on chemical reactions. This work is written with this in mind. Its objective is to present technical details of the different possibilities to characterize surfaces by AFM and, when possible, to show the applications of these techniques to chemistry and biology. It is not pretended that this contribution is a complete picture of the AFM world and neither gives an exhaustive presentation of technical details. What is pretended is to guide the non-expert through different possibilities of characterization by AFM.

This work starts with the principles of AFM in which is explained how tip–surface interactions are measured. Then, it is followed by a description of the different modes, contact, non-contact, and intermittent mode to obtain topography from a micro-size to atomic resolution. Subsequently, the main topic of this contribution is presented by mentioning the different measurements that can be done, such as forces between a functionalized tip and surfaces, mechanical properties such as friction and stiffness, electrical properties such as surface potential, electric polarization and surface charge, electromechanical properties such as piezoelectricity and electrostriction, and

Dedicated to Professor Janos H. Fendler (Clarkson University, USA) on the occasion of his 70th birthday.

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magnetic properties of materials. A brief summary concludes this review.

Principles

An AFM is composed of several parts to be able to extract topography from surfaces. There are components that are not missed in any system like a very small radius tip on a cantilever with a low spring constant, a technique to measure cantilever deflections produced by forces between the tip and the surface, a scanning capability in three dimensions that makes the tip move relatively on the surface, a feedback system to obtain topographic or other type of information, and a software that can interpret data as image.

Nowadays, there are a great number of cantilevers and tips that are in use. Some of the most common are those made with silicon and silicon nitride. There are silicon cantilevers that have rectangular shape with spring constants from small as 0.1 N/m to cantilevers with 40 N/m. The triangular silicon nitride cantilevers more suitable for contact mode have spring constants from 0.01 to 0.58 N/m (Veeco Metrology, Santa Barbara, CA). The tip radius varies from 10 to 20 nm for the silicon nitride tips and around 10 nm for the silicon tips, although there are special high aspect ratio probes that tip radius as small as 1 nm.

In the young history of AFM, there have been a number of deflection systems that have been used like the pioneer scanning tunneling tip on top of the AFM cantilever to measure displacements [1]. However, the three most used techniques are the laser reflection method, interferometric method, and the piezoresistive method.

In the laser reflection method, a laser beam is reflected from the cantilever surface and directed to a two- or four-quadrant photodetector. The difference in signal from the different parts of the photodetectors is used as a way to measure deflection of the cantilevers [3]. As seen in Fig. 1, any vertical deflection of the cantilever produced by the interaction between the tip and the surface makes the beam to be reflected higher or lower on the detector. The light hitting any part of the detector is transformed to current, so there are four independent light sensors and four different currents that can be used. The amount of current from the top part (1+2) minus the amount of current from the bottom part (3+4) is a signal proportional to the vertical motion of the cantilever. This detector method is the most popular in commercial systems.

In the interferometric method, the optical path difference between a beam that is reflected from the interface of the fiber-air and the beam that is reflected at the back of the cantilever is used to detect deflections [4]. The method was independently proposed by Martin et al. [5] and Erlandsson et al. [6], although simpler arrangements are now in used [4]. Only 4% of the light is reflected on the fiber–air interface and the rest is transmitted to the back of the cantilever, but that amount is enough to produce the interference between the two beams and then the measurement of deflection.

Piezoresistivity is a property of certain materials that change its resistivity by stress. This property can be used to measure deflections [7]. A cantilever is coated with a piezoresistive material, and the film is connected in a Wheatstone bridge acting as one resistor. A voltage V is applied to the bridge. As the resistance of the film changes with deflection, then the current going through changes accordingly. This current through the film on the cantilever is taken as a measurement of deflection.

In any mode to obtain topography, the tip is moved following the surface. This motion or scanning is done by piezoscanners. A piezoscanner is a device made with piezoelectric materials, materials that are extended or contracted by voltages, which by a controlled way is made to scan the sample in a rectangular way with a fast and a slow axis. The scanner also moves the cantilever up or down to obtain topography of the sample.

Most AFM imaging modes involve a feedback loop which regulates the tip–sample distance. As shown in Fig. 1, the signal processing circuit produces a signal that is compared to the set point generating an error signal. In contact mode, the compared signal is the cantilever deflection, whereas in tapping mode, the signal is the amplitude of the cantilever oscillation. The signal from the processing circuit is subtracted from the set point and the result, the error signal, is the input of a feedback calculation. The result of this calculation is then used to

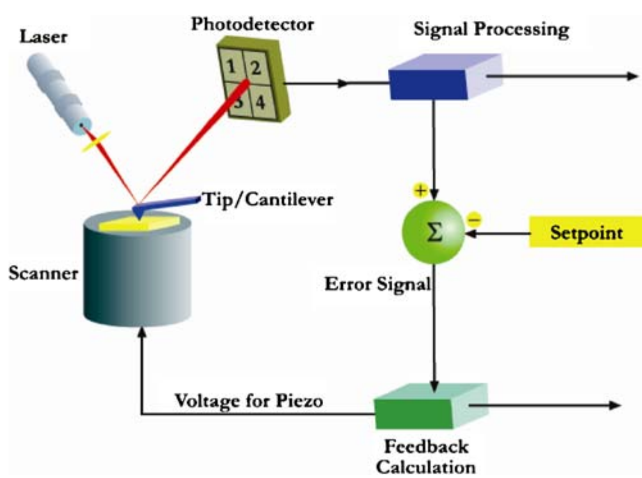

Fig. 1 Laser reflection method and schematics of a feedback loop. Any vertical deflection of the cantilever is measured by the signal composed by subtracting the photocurrent on the bottom of the detector (3+4) from the photocurrent on the top of the detector (1+2). The feedback circuit keeps the error signal equal to zero

control the tip–sample separation through a high-voltage amplifier and fed to a piezoscanner that changes the tip–sample separation. The job of the feedback calculation is to keep the error signal equal to zero. The output of the feedback calculation is a representation of the sample topography or height.

The software of the AFM has the following features: (1) able to control the scanning, feedback, and the acquisition of data, (2) able to convert data points into pixels for an image, and (3) able to manipulate images to transform, present, or make calculations.

Topography

Every AFM system is used for topography, that is, to reproduce surface landscape as an image. There are three basic modes in AFM in which topography can be obtained: contact mode, non-contact mode, and tapping mode. The modes are applied in every field in science. Topography can be taken in air (contact and tapping), liquid (contact and tapping), and in vacuum (contact and non-contact).

Contact mode is the region of strong repulsive forces between the tip and the surface, the non-contact mode is the region of weak attractive forces, and the tapping mode is the region in between; that is, the interaction between the tip and the surface is in the contact region for a short time (a "tap") but is in the non-contact region most of the time.

In the contact mode, there are two basic ways to obtain topography: constant force mode, which is a constant deflection mode, and variable force mode, which is a free deflection mode.

The schematic for the contact force mode is shown in Fig. 1. The signal compared to obtain the error signal consists in the top minus bottom or (1+2)–(3+4) signal, that is, the deflection of the cantilever. The feedback loop compares the deflection signal to the set point and changes the voltage applied to the height, *z*, part of the scanner, to maintain the deflection constant. As seen in Fig. 2a, topography is actually the voltage applied to the scanner.

The variable force mode is a contact mode for presumably atomic resolution. In this mode, the feedback loop is disabled. As seen in Fig. 2b, the tip scans the surface horizontally leaving the cantilever free to deflect following the topography of the surface. Height is the deflection signal of the cantilever. This technique should be used in very small scan sizes because, otherwise, the tip and/or the sample could be damaged with large changes in height on the surface that will produce a large deflection on the cantilever.

In the non-contact mode region, Van der Waals forces are in effect. Some other forces could be in action such as electrical and magnetic forces. However, if the surface is not charged and if the surface and tip are not ferromagnetic, the predominant forces are Van der Waals. The schematic of non-contact mode is presented in Fig. 3. Away from the surface, the cantilever is made to oscillate close to its resonance frequency with certain amplitude. When the tip is close to the surface, the gradient of the total force on the tip acts as an additional spring on the cantilever, so that it changes its resonant frequency. Its change in resonance frequency makes the cantilever oscillate at lower amplitude, as the driving frequency is maintained constant. Because a lock-in amplifier is an amplifier that measures the signal at the reference frequency and filters practically any signal at other frequencies, then it is used to measure the amplitude of oscillation of the deflection signal at the driving frequency. The deflection signal is then fed to the lock-in

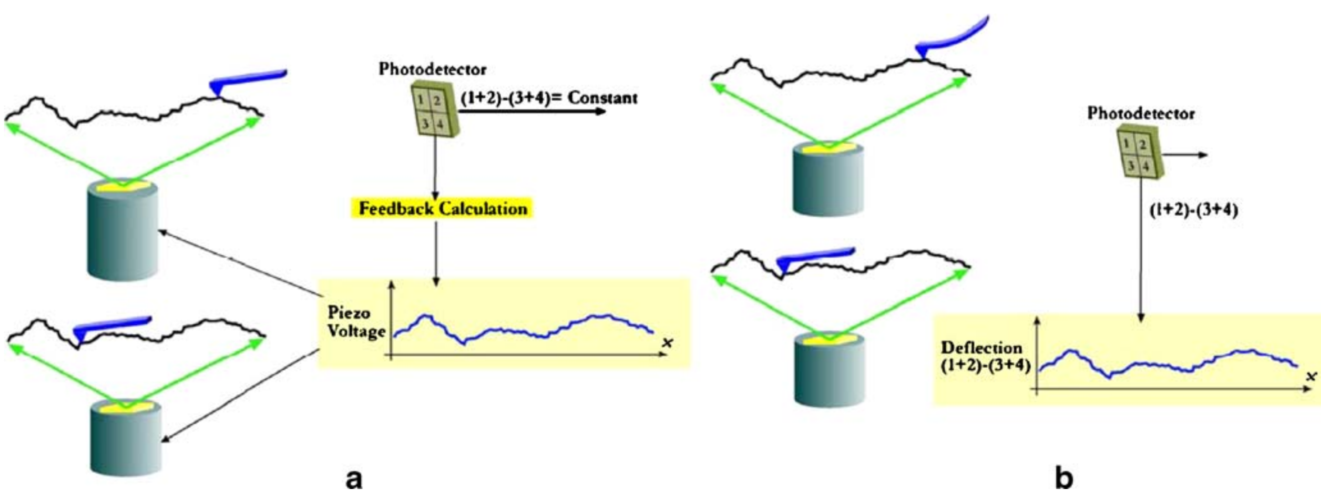

Fig. 2 Contact modes. **a** Constant force mode. The deflection signal (1+2)−(3+4) is taken for the error signal. The circuit maintains that signal equal to the setpoint. To do that the feedback loop circuit changes the piezovoltage to maintain a constant deflection. The piezovoltage is taken as topography. **b** Variable force mode. In this mode the feedback loop is disabled. When the tip scans the surface, the cantilever is free to deflect following the surface. The deflection of the cantilever is taken as topography

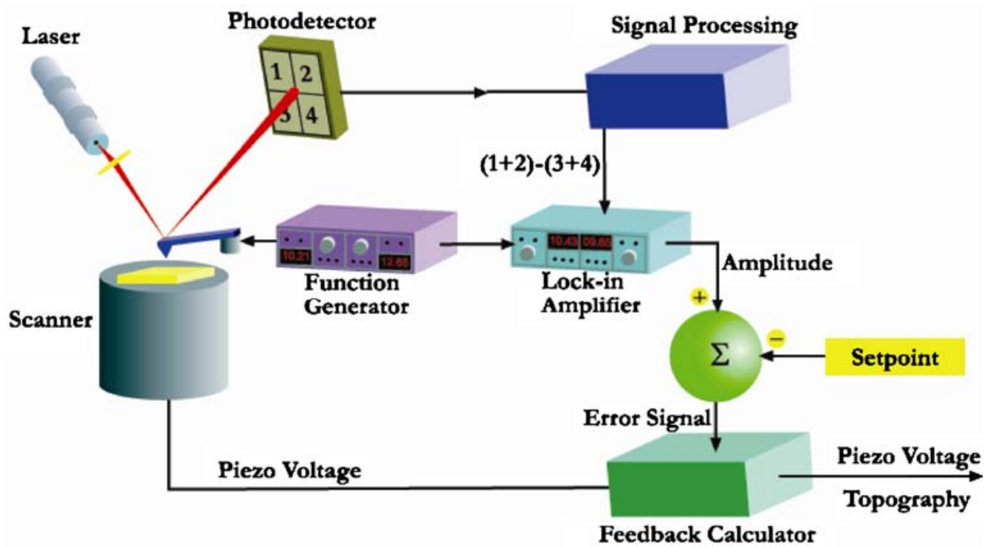

Fig. 3 Non-contact mode. The amplitude of oscillation is measured by a lock-in amplifier. The error signal is the difference of the amplitude of oscillation and the set point. The piezovoltage, as in the constant force mode, is topography

amplifier, and the driving frequency of oscillation is used as reference. In this mode, the amplitude of oscillation is the signal compared to the set point to obtain the error signal so that the feedback loop maintains the amplitude equal to the set point changing the voltage in the piezoscanner and then maintaining a constant tip-surface distance. As in constant force mode, topography is the voltage applied to the piezoscanner. The main advantage of non-contact mode compared to contact mode is that, as the tip is always in the weak attractive region, the sample and tip are not easily damaged.

There is still another non-contact mode that is used in vacuum environments, the frequency modulation dynamic mode [8]. This mode has greater sensitivity in the attractive region by an order of magnitude. It is operated at a moderate vacuum, which makes the quality factor, Q, of the cantilever higher. The cantilever serves as the frequency determining element by force gradients acting on it. The driving signal of the cantilever comes from a feedback loop in which the vertical detector signal is amplified and phase shifted to ensure maximum positive feedback. The degree of amplification is determined by an automatic gain controller that makes sure the amplitude of oscillation is constant. The images come from the measurement of the oscillation frequency of the cantilever by constant shift in oscillation frequency moving the tip up and down by controlling the average tip–sample distance. Therefore, the topography is actually a constant frequency shift map, which differs from a constant amplitude shift map in amplitude modulated AFM.

Tapping mode is a technique in which the tip–surface interaction is in the contact and the non-contact region intermittently [9]. It is also called intermittent contact mode. The two names are synonymous. It is an amplitude modulation dynamic mode in both contact and non-contact regions. Its hardware is the same as the non-contact mode presented in Fig. 3. This mode in air has better resolution than the non-contact mode, and it has its same advantage as compared to contact mode, i.e., the sample is not damaged. Nowadays, tapping mode is more used than the non-contact mode because its control is easier. In fact, many of the early reported non-contact experiments were actually tapping mode experiments.

Non-topography measurements

AFM is not only used for topography but also for obtaining property information. The physical properties that have been measured include mechanical, electrical, and magnetic properties. In addition, there are a number of electromechanical and magnetomechanical properties that have been measured using AFM.

Forces

Forces in AFM are measured by the deflection of the cantilever. If a force is measured vs the tip–surface distance, then the result is called a force spectroscopy. A scheme of a resultant curve is shown in Fig. 4. There are several regions in a resultant curve as depicted in the figure. From *a* to *b*, the cantilever is not deflected because the attractive force is small. From *b* to *c*, suddenly, the total force gradient on the cantilever is greater than its spring constant, so it "jumps" to contact. From *c* to *d*, the tip is in contact with the sample. The slope is a measure of sample–tip stiffness. An estimation of the point of tip–sample contact can be obtained by the intersection of the contact and the non-contact regions of the force curve [10]. The elastic modulus and plasticity of samples can be obtained from the corrected

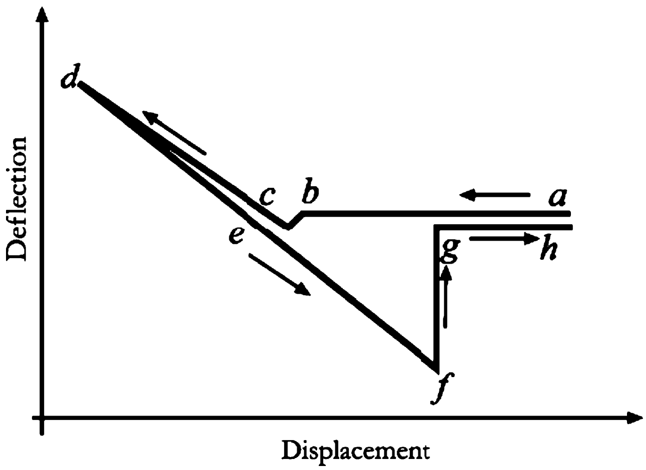

Fig. 4 A schematic of a force–distance curve of the interaction of the tip and surface

slope of the force curve after contact from *c* to *d* [11]. At *d*, the control starts separating the tip and sample. If the slope from *d* to *e* is different from the slope from *c* to *d*, then deformation is present. From *e* to *f*, there is an attraction force due to capillarity forces or other adhesion forces. From *f* to *g*, the gradient of the force on the cantilever is greater than its spring constant and the cantilever is released from the surface, and from *g* to *h*, the cantilever is not deflected.

In colloidal studies, particles are typically attached to the end of AFM cantilevers by micromanipulators under an optical microscope. Since the availability of tip-less cantilevers, the size of the particle is only limited by the attachment procedure. In a recent work, it has been possible to attach 1-μm-diameter particles. The majority of colloid probe studies are on the interaction between a sphere and a flat surface, but there are studies of the interaction between two spheres [12]. Spheres can be attached to a substrate in the same way as to a cantilever or deposited on an adhesive surface.

As force spectroscopy has a series of properties that are locally measured, one of these force curves can be performed at each pixel to have a series of images where each measurement of a deflection is recorded. When all the measurements for a pixel are completed, the process is repeated at the next point and so on with all of them in the area. The resulting maps represent the variation of adhesion force due to material inhomogeneities and the surface topography [13]. This technique is called force imaging microscopy.

In a particular case of force imaging microscopy, tips have been functionalized to measure intermolecular forces [14, 15] calling this technique chemical force microscopy. A force measurement is made by moving the probe and substrate together and monitoring cantilever deflection as a function of displacement. Furthermore, with functionalized tips, research in adhesion [16] and in friction [17] has been performed. Measurement of nanometer-scale tribological phenomena [18] has been achieved.

Force spectroscopy has been used in Biology to calculate the Young modulus of cells by analyzing force curves [19]. Mechanical properties of erythrocytes from patients with different diseases were compared to those of erythrocytes from healthy persons, obtaining that the Young's modulus of pathological cells was higher than that of normal erythrocytes. Because of its capability to image nanometer-sized topography, together with its capability to measure molecular-level forces, the AFM has become a tool to simultaneously obtain topographic details and have molecular recognition in a biological sample under near-physiological conditions [20].

Mechanical properties

Among the mechanical properties that have been obtained by AFM, friction is one of the most studied properties. Friction can be obtained by three techniques: lateral force mode [21], lateral force modulation [22, 23], and torsional resonance mode [24].

Lateral force mode became a widely used technique when it was proved that both topography and friction could be obtained by the laser reflection detection [25]. The technique is quite easy to implement, as nowadays, most commercial systems have this detection system and the detector they used is a quadrant detector, which means that the detector is divided into four quadrants and current on each quadrant can be isolated or combined. In this type of systems, as shown in Fig. 1, signal (1+3)−(2+4) is a measurement of how much the cantilever is twisted. When a tip scans the surface in contact, the cantilever is twisted by two effects: friction and topography. The difficulty of this technique is to differentiate one effect from the other. The tip is twisted when it goes up or down in a hill due to topography. In addition, the tip is twisted by friction, and differences in the friction coefficient between the tip and the surface will produce different torsions of the cantilever. The way to eliminate the topographic component of the torsion is by using both the lateral signal when the tip goes in one direction (forward) and when it comes back in the same line (backward). In forward and backward directions, the lateral signal due to topography has the same contour, whereas the signal due to friction is reversed. Subtracting the backward signal from the forward signal eliminates the topographic part of the lateral signal, leaving just the frictional part. For qualitative analysis of surfaces, this subtraction can be taken as friction measurements, although much more careful analysis of the signals, experimentally and mathematically, it is far from being correct. Quantitative analysis needs to take into account that this subtraction remains dependent on topography, and more careful data computation has to be done. Topographic and friction coefficient images in micro-sized regions, where hills and valleys are dense, were obtained by friction force microscopy (FFM) in lead zirconate titanate (PZT) thin films (see Fig. 5). In the friction image, Fig. 5b, the brightness is scaled to the measured friction coefficient. As can be seen, both hills and valleys appeared as regions where the friction coefficient was smaller than the rest of the film. The unit nA is just a relative unit that is proportional to the actual friction coefficient.

Lateral force modulation was independently proposed in an interferometric detection system [22] and in a laser reflection detection system [23]. The idea is to make the surface to laterally oscillate when the tip is in contact. Feedback is attained by the deflection of the cantilever as the normal contact mode. The lateral signal is now modulated to the frequency of the surface oscillation. A lock-in amplifier measures the amplitude and phase of the tip torsional modulation, which are related to the friction and elastic properties of the surface. For large amplitudes of surface oscillation, friction is measured, and for small amplitudes, elastic properties are measured.

Using the idea of lateral force modulation, the torsional resonance mode was born [24]. Rather than the surface, in this mode, the tip is made to oscillate. The lateral signal is fed to a lock-in amplifier. The amplitude of the signal can be used as a feedback signal, and in that case, there is no need of the vertical signal. To do this, the cantilever needs to be oscillated in its torsional resonance frequency, and the change in cantilever oscillation amplitude is used as a parameter of feedback. This is why the authors named this technique as torsional resonance mode. If the normal vertical signal is used for feedback, then the amplitude and phase of the lateral signal modulation is used as a measure of friction. Preliminary experimental results and theoretical analysis have predicted that, by using torsional resonance mode, one will be able to acquire quantitative measurements of surface friction and stiffness [26].

FFM, in any of its versions presented, is a technique that can provide important information of materials. Although it is difficult to make quantitative analysis, qualitative analysis indicates that it is sensible enough to distinguish molecular composition and surface composition in organic materials in a nanometer spatial resolution. When combined with the control of the tip chemistry, deeper understanding of compositions of organic molecules could be obtained beyond what can be obtained with other analytical techniques [27]. A great review has been written using FFM with self-assembled monolayers [28].

Stiffness is another widely studied property. One of the most used techniques for this is force modulation microscopy [29]. The tip is in contact and normal feedback is attained by the vertical deflection. However, the cantilever oscillates vertically at a certain frequency. This oscillation is modulated by the mechanical properties of the surface, and the vertical signal is fed to a lock-in amplifier to detect amplitude and phase of the oscillation of the cantilever. Depending on the surface, the amplitude will be greater for hard surfaces or lower for soft surfaces. This technique is standard in most commercial systems.

There are two techniques that are similar, one called ultrasonic AFM [30] and the other ultrasonic force microscopy (UFM) [31]. In both techniques, a low frequency modulated ultrasonic wave is sent through the cantilever in the first and through the sample in the second. In both cases, the cantilever is in contact with the surface, and the ultrasonic wave makes the vertical deflection signal of the detector to be modulated at the low frequency, which amplitude and phase will depend on the mechanical properties of the sample.

Recently, UFM has been applied to measure adhesion hysteresis of two types of proteins in different conditions of humidity using a controlled humidity environment by means of a dry-box [32]. Adhesion hysteresis curves are composed of tip–surface inherent adhesion hysteresis and capillarity force hysteresis. The latter is very humidity-dependent. In this work, it was proved that UFM is

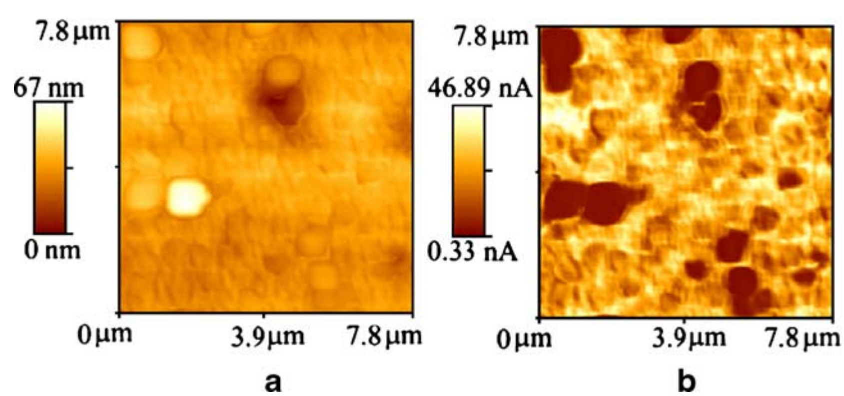

Fig. 5 Lateral force microscopy image. Topography (**a**) and the corresponding friction image (**b**) from a PZT thin film

sensitive enough to distinguish different proteins in low humidity and that local water-protein binding capacity in a protein could be obtained with a nanometer resolution limited by the tip–surface contact radius.

Tapping mode AFM has also been used to map tip–surface interactions. The cantilever oscillates at its resonant frequency at a position just above the surface, so that the tip is in contact with the surface for only a very short time. A feedback loop forces that the amplitude of the cantilever oscillation remains constant using a lock-in amplifier. As it is possible to measure the phase difference between the driving oscillation and the detected cantilever oscillation, a phase difference map can be obtained. An increase in the phase difference arises from a stronger tip–sample interaction creating contrast in the phase map. Using tapping mode to obtain mechanical properties has been explained elsewhere [33].

Recently, frequency modulated AFM or non-contact mode in vacuum and low temperature has been used to report direct force measurements of the formation of a chemical bond on a silicon (111) 7×7 surface [34].

Electrical and electromechanical properties

Some electrical properties have been obtained by AFM. In contact mode, conductivity measurements have been realized [35] by applying a potential between the tip and the bottom electrode of the sample and measuring the current through the tip by a low-noise amplifier. In tapping mode, also conductivity measurement have been done by the same principle that the tip is in contact some of the time [36]. In non-contact charge, either free charge or polarization charge, potential, and capacitance have been obtained.

In non-contact, the main interaction between the tip and the surface is by the Van der Waals forces. This is true if neither electrical nor magnetic forces are present. If electrical interactions are present, electric forces will dominate Van der Waals forces because those forces decay slower. One technique that one can use is simply oscillating the tip at a certain distance from the surface and the electrical interaction between the tip and the surface will change the amplitude and phase of oscillation as van der Waals do in normal non-contact mode. However, this is not done frequently. A better technique is to apply a combination of a dc and ac voltage with a certain frequency between the tip and the bottom electrode of the sample, $V = V_{dc} + V_{ac}\sin(\omega t)$. If the surface is conductive, then the force on the tip will be composed of a dc part $F_{\mathrm{dc}} = -\frac{1}{2}\frac{\partial C}{\partial z}\left[\left(V_{\mathrm{cpd}} + V_{\mathrm{dc}}\right)^2 + \frac{1}{2}V_{\mathrm{ac}}^2\right]$, a force modulated at the frequency, $F_\omega = -\frac{\partial C}{\partial z}\left(V_{\mathrm{cpd}} + V_{\mathrm{dc}}\right)V_{\mathrm{ac}}\sin(\omega t)$ and a force modulated at the double of the frequency, the second harmonic, $F_{2\omega} = \frac{1}{4}\frac{\partial C}{\partial z}V_{\mathrm{ac}}^2\cos(2\omega t)$ where $\frac{\partial C}{\partial z}$ is the derivative of the capacitance of the tip–surface with respect to the tip–surface distance and V_{cpd} is the contact potential difference between the tip and the conducting surface.

Scanning Kelvin probe microscopy [37, 38] uses this principle to measure the contact potential difference so that the local work function of the sample can be obtained. Because the force on the tip is modulated, then the vertical oscillation will be also modulated in ω and 2ω. A lock-in amplifier measures the amplitude of the vertical deflection at frequency ω. Using a feedback loop, this amplitude can be forced to be zero by applying a dc voltage that equals the negative of the contact potential difference. In this way, the applied dc voltage is the measurement of the contact potential difference.

The advantage of the scanning Kelvin probe microscopy is, as any other non-contact technique, its non-invasive way of characterization with a nanometer-scale resolution. It has been used to probe phase separation, as coexisting monolayers will have different effects on the contact potential difference between the tip and the bottom electrode, given the difference in their dielectric constant and thickness, and to recognize different chemical entities and molecular orientation [39].

If the sample is not conducting, the same technique, applying an ac voltage, can be used. In this case, the first harmonic amplitude is proportional to the amount of charge on the surface, and phase is a measurement of the type of charge. This can be done with free charge [40] and with polarization charge in a ferroelectric surface [41]. Regions of a ferroelectric film were polarized by applying either positive or negative voltages with the AFM tip. A typical experiment is illustrated in Fig. 6. On three points, a positive voltage was applied (points 1, 2, and 3 in b), and on two points, a negative voltage was applied (points 4 and 5 in b). After the voltage was applied, the region was scanned in the non-contact mode, measuring the magnitude and phase of the first harmonic signal along with the topography. In Fig. 6b, the magnitude, all of five points are clearly shown. In Fig. 6c, the phase, the two negative-voltage-applied points showed 180° out of phase signals suggesting surface positive charge. The three positive-voltage-applied points showed zero phase signals. This phase indicates that the three points had a negative surface charge.

With the second harmonic, one can obtain images that are qualitatively related to the capacitance of the tip–surface [42]. To make quantitative analysis, one has to make spectroscopy measurements, that is, second harmonic amplitude vs distance curves to integrate and obtain capacitance [41]. A better approach of today's capacitance microscopes is to use an independent capacitance sensor (like the RCA type of sensor) that measures capacitances at high frequencies along topography [43].

The most used of the techniques presented above in electrical characterization, by far, is Kelvin probe force

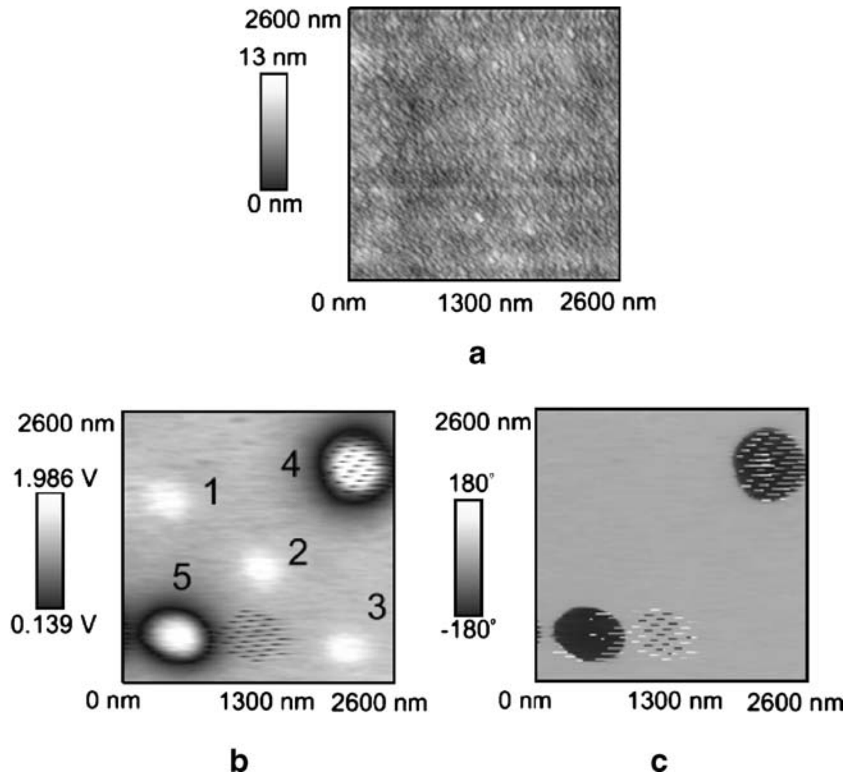

Fig. 6 **a** Topography, **b** magnitude, and **c** phase of polarization signal for a region where five points were polarized. 1, 2, and 3 in **b** are positive-voltage-applied points, and 4 and 5 are negative-voltage-applied points

microscopy (KPFM). A very complete review of the possibilities of the use of KPFM in characterizing electric properties of organic semiconductors, organic monolayers, supramolecular systems, and biology has been published elsewhere [44]. The same group of investigators recently published a detailed study of characterization by KPFM of perylenebis-dicarboximide films, an organic semiconducting nanostructure [45]. The study consisted on the measurement of surface potentials in different experimental conditions such as amplitude, frequency, and phase of the voltage applied, as well as the tip–surface distance. A theoretical model that takes into account the contribution of a dipole barrier due to the tip-induced polarization of the sample on the measured surface potential, which is tip-sample dependent, is used and its results are in good agreement with experimental data.

Electromechanical properties such as electrostriction [46] and piezoelectricity [47] have been obtained locally by the AFM using basically the same technique. A conductive tip is used, and a regular feedback technique in the contact mode is used. An ac voltage is applied between the tip and the bottom electrode of the sample to drive mechanical movements, i.e., from electrostriction or piezoelectric response of the film. The position of the reflected beam on the cantilever surface is detected by the four-segment detector. The signal (1+2)−(3+4), which

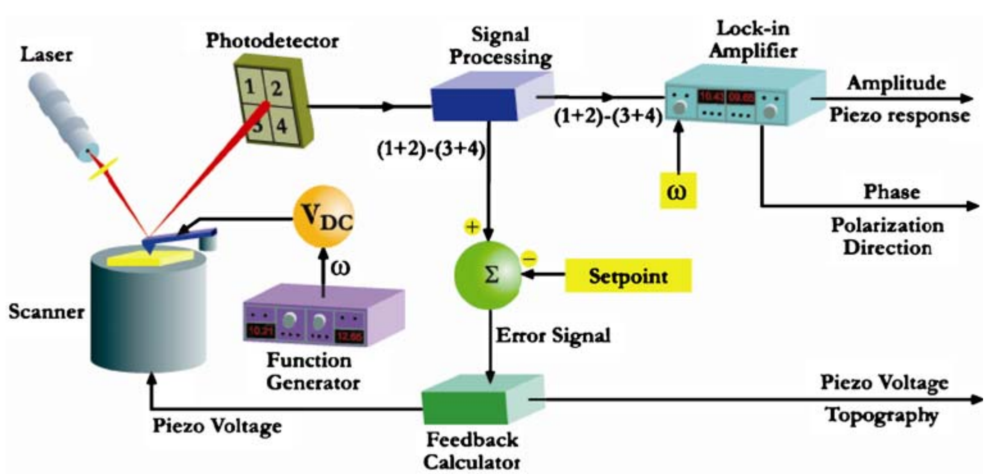

Fig. 7 Piezoelectric measurements are performed by applying an ac voltage to the sample through the tip. Local strain of the sample is measured by the deflection of the cantilever

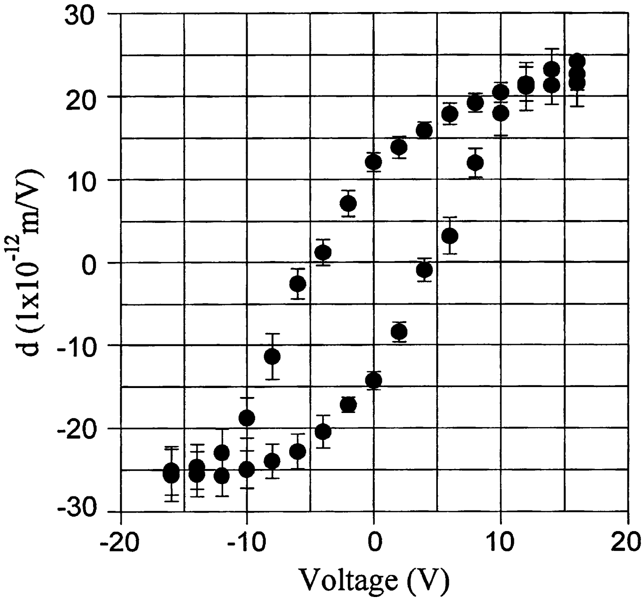

Fig. 8 Piezoelectric loop taken by measuring the vibration of the tip at a frequency of an applied ac signal on a piezoelectric thin film

detects any vertical movement, is taken to a lock-in amplifier, which is referred to the frequency of the voltage applied as shown in Fig. 7 that shows a scheme of piezoelectric measurements. In the case of electrostriction, the frequency reference of the lock-in amplifier is twice the frequency of the applied voltage. With piezoelectric measurements, an additional dc voltage can be applied to polarize ferroelectric samples and piezoelectric loops can be obtained [41]. In this case, the phase is related to the direction of polarization. A piezoelectric loop (see Fig. 8) was obtained by means of a computer-controlled experiment. The piezoelectric response was measured for different polarization voltages in a PZT thin film. For each measurement, the piezoelectric constant (*d*) was set to be negative when the phase obtained was 180° and positive when the phase obtained was 0°, indicating the main orientation of the domains. The resulting curve had all the features of a hysteresis loop; *d* values came to a saturation point around 13 V and the coercive voltage (Vc) was around 3–4 V (similar to the ferroelectric loop hysteresis obtained on the same film).

Magnetic-related properties

With a magnetic coating of a tip and a magnetic sample, magnetic forces dominate Van der Waals forces in non-contact, so a magnetic force microscope can be achieved [48, 49]. The technique is normally used by taking topography first by tapping mode. The topography is recorded, and the tip is taken away from the surface and scanned at constant distance from the surface following the stored topography. In this second scan, the cantilever is oscillating at resonance frequency. The magnetic force on the cantilever changes its resonance frequency. The amplitude and phase of the oscillation is measured by a lock-in amplifier giving a measurement of magnetic force. If the magnetic moment of the tip is short, the magnetic force is proportional to the gradient of the magnetic field of the sample. If the magnetic moment of the tip is long, then the magnetic force is proportional to the field produced by the sample. However, in both cases, the amplitude of oscillation of the cantilever is proportional to the gradient of the force, making magnetic force images difficult to interpret. Figure 9 shows the topographical image obtained by AFM and the phase image obtained by magnetic force microscopy at the same time of nickel particles. The particles were magnetized in a longitudinal direction to obtain a magnetic signal. From the MFM image in Fig. 9, it can be observed that the signal obtained shows the typical pattern of single domain longitudinal magnetization. However, it can also be appreciated that not all the particles have their magnetization on the same direction. This could be due to the influence of their neighbors and their different sizes.

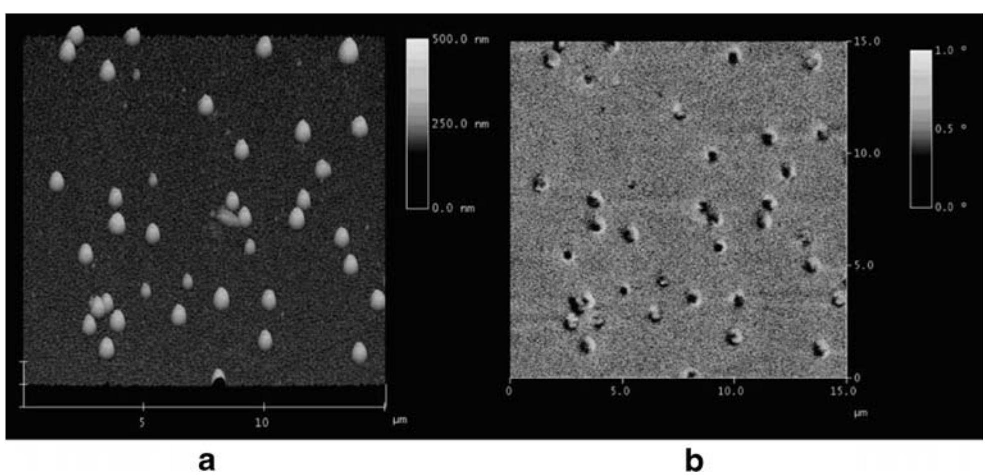

Fig. 9 **a** AFM image of the topography of the sample. The particles show a nearly hemi-spherical morphology. **b** MFM image on the same area. It can be seen that the particles have a single domain longitudinal magnetization

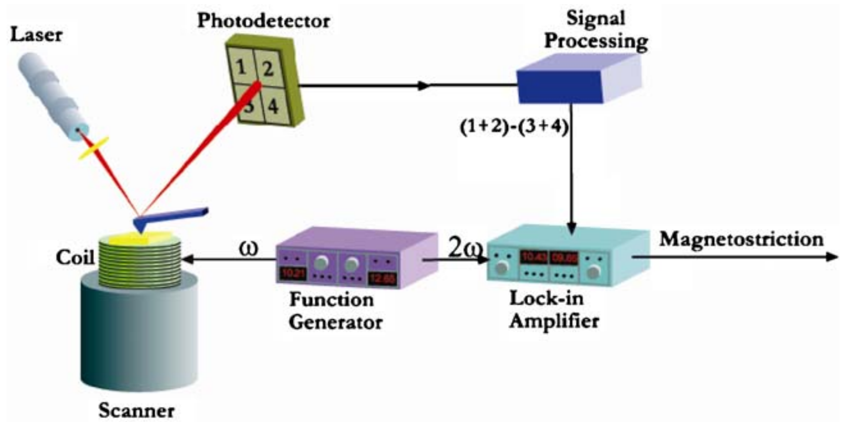

Fig. 10 Magnetostriction is measured by applying a varying magnetic field to the sample while measuring the sample strain by the deflection of the cantilever

The only magnetomechanical property that has been measured is magnetostriction [50]. This is realized by applying an ac magnetic field in situ and measuring strains by a non-magnetic tip as shown in Fig. 10. Because magnetostriction is the change of strain proportional to the square of an applied magnetic field, the lock-in amplifier is referred with twice the frequency of the ac magnetic field applied to the sample.

Magnetoresistive properties have been measured only indirectly by obtaining magnetic force images at different temperatures including the temperature of percolation [51] and by doing conductivity measurements at different temperatures including the temperature of percolation [52].

Other uses

Another important application of AFM is that it can be used on in situ chemical reactions that can be characterized in the nanometer scale. There are two types of chemical reactions using the AFM, those in which the tip is just an observer of the process and those in which the tip participates in the chemical reaction process. Several manufacturers have produced electrochemical cells in which the tip can be used to image the process while the chemical reaction is taking place such as in corrosion studies [53]. By applying voltage pulses to the tip, an oxidation of surfaces can take place as firstly demonstrated by Day and Allee [54]. The process of local oxidation of surfaces is understood as having a nano-sized electrochemical cell formed by the tip as cathode and the water meniscus formed on the tip–surface contact as the electrolyte as stated recently on a comprehensive review of nanolithography techniques by AFM [55].

Figure 11 shows a corrosion experiment in situ in an electrochemical cell in which the tip does not participate in the process; it scans the topography. The experiment consists on increasing the potential between the working and reference electrode in a 0.167 mV/s rate while measuring the current on the counter electrode to determine the pitting potential, which in this case is the potential when the current density reaches 100 μA/cm^2. During the experiment, a series of topographic images were taken.

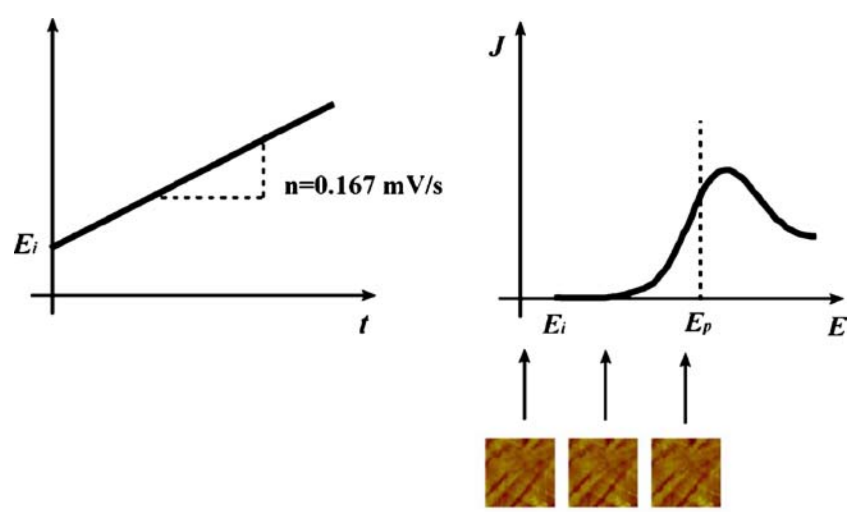

Fig. 11 A corrosion experiment performed in an atomic force microscopy electrochemical cell in which the tip is scanning topography while the corrosion process is occurring

Summary

The work presented a general review of techniques available in atomic force microscopy. A section of the basic principles to understand the capabilities of AFM was offered. A detailed description of the different interactions that are used to measure physical properties of materials was presented in the main section of this contribution and applications within several fields were mentioned and cited. The main advantage of this instrument is that possibilities of new AFM techniques are far from being exhausted. New techniques and new ways to characterize materials are coming every moment. The application of techniques available and techniques to come will make tremendous contributions in physics, materials science, chemistry, and biology. At the same time, these new techniques jointly with the old techniques are posing new challenges that are difficult to approach. The need for better scanners and better tips is evident to characterize, in a reliable way, a single nanoparticle or a molecule. Better scanners are needed to spatially control the tip position and tips to control the type of interaction as well as to decrease the area of interaction. Nevertheless, the field is open, as the only limit is the imagination.

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References

1. Binnig G, Gerber C, Quate C (1986) Phys Rev Lett 56:930
2. ISI Web of Science (2006) http://scientific.thomson.com/products/wos/. Cited 1986–2006
3. Meyer G, Amer NM (1988) Appl Phys Let 53:1045
4. Rugar D, Mamin HJ, Guethner P (1989) Appl Phys Lett 55:2588
5. Martin Y, Williams CC, Wickramasinghe HK (1987) J Appl Phys 61:4723
6. Erlandsson R, McClellan GM, Mate CM, Chiang S (1988) J Vac Sci Technol A 6:266
7. Tortonese R, Barrett RC, Quate CF (1993) Appl Phys Lett 62:834
8. Albrecht TR, Grutter P, Horne D, Rugar D (1991) J Appl Phys 69:668
9. Zhong Q, Inniss D, Kjoller K, Elings VB (1993) Surf. Sci Let 290:L688
10. Radmacher M, Cleveland JP, Fritz M, Hansma HG, Hansma PK (1994) Biophys J 66:2159
11. Mareanukroh M, Eby RK, Scavuzzo RJ, Hamed GR, Preuschen J (2000) Rubber Chem Technol 73:912
12. Rutland MW, Carambassis A, Willing GA, Neuman RD (1997) Colloids Surf A 369:123
13. Rotsch C, Radmacher M (1997) Langmuir 13:2825
14. Frisbie CD, Rozsnyai LF, Noy A, Wrighton MS, Lieber CM (1994) Science 265:2071
15. Vezenov DV, Noy A, Ashby P (2005) J Adhesion Sci Technol 19:313
16. Vezenov DV, Noy A, Rozsnyai LF, Lieber CM (1997) J Am Chem Soc 119:2006
17. Green J-B, McDermott MT, Porter MD, Siperko LM (1995) J Phys Chem 99:10960
18. Roggemann MC, Williams JG (2002) J. Adhesion Sci Technol 16:905
19. Dulinska I, Targosz M, Strojny W, Lekka M, Czuba P, Balwierz W, Szymonski M (2006) J. Biochem Biophys Methods 66:1
20. Kienberger F, Ebner A, Gruber HJ, Hinterdorfer P (2006) Accounts Chem Res 39:29
21. Mate CM, McClelland GM, Erlandsson R, Chiang S (1987) Phys Rev Lett 59:1942
22. Goddenhenrich T, Muller S, Heiden C (1994) Rev Sci Instrum 65:2870
23. Yamanaka K, Tomita E (1995) Jpn J Appl Phys 34:2879
24. Huang L, Su C (2004) Ultramicroscopy 100:277
25. Meyer G, Amer N (1990) Appl Phys Lett 57:2089
26. Reinstadtler M, Kasai T, Rabe U, Bhushan B, Arnold W (2005) J Phys D Appl Phys 38:R269
27. Leggett GJ, Brewerb NJ, Chong KSL (2005) Phys Chem Chem Phys 7:1107
28. Leggett GJ (2003) Anal Chim Acta 479:17
29. Maivald P, Butt HJ, Gould SAC, Prater CB, Drake B, Gurley JA, Elings VB, Hansma PK (1991) Nanotechnology 2:103
30. Yamanaka K, Nakano S (1996) Japan J Appl Phys 35:3787
31. Kolosov OV, Castell MR, Marsh CD, Briggs GAD, Kamins TI, Williams RS (1998) Phys Rev Lett 81:1046
32. Szoszkiewicz R, Kulik AJ, Gremaud G, Lekka M (2005) Appl Phys Lett 86:123901
33. Garcia R, Perez R (2002) Surf Sci Rep 47:197
34. Lantz MA, Hug HJ, Hoffmann R, van Schendel PJA, Kappenberger P, Martin S, Baratoff A, Güntherodt H-J (2001) Science 291:2580
35. O'Shea SJ, Atta RM, Murrell MP, Welland ME (1995) J Vac Sci Technol B 13:1945
36. Luna M, de Pablo PJ, Colchero J, Gomez-Herrero J, Baro AM, Tokumoto H, Jarvis SP (2003) Ultramicroscopy 96:83
37. Weaver JMR, Abraham DW (1991) J Vac Sci Technol B 9:1559
38. Nonnenmacher M, O'Boyle MP, Wickramasinghe HK (1991) Appl Phys Lett 58:2921
39. Fujihira M (1999) Annu Rev Mater Sci 29:353
40. Terris BD, Stern JE, Rugar D, Mamin HJ (1989) Phys Rev Lett 63:2669
41. Zavala G, Fendler JH, Trolier-McKinstry S (1997) J Appl Phys 81:7480
42. Martin Y, Abraham DW, Wickramasinghe HK (1998) Appl Phys Lett 52:1103
43. Barrett RC, Quate CF (1991) J Appl Phys 70:2725
44. Palermo V, Palma M, Samori P (2005) Adv Mater 18:145
45. Liscio A, Palermo V, Gentilini D, Nolde F, Müllen K, Samori P (2006) Adv Funct Mater 16:1407
46. El Hami K, Yamada H, Matsushige K (2001) Appl Phys A 72:347
47. Guthner P, Dransfeld K (1992) Appl Phys Lett 61:1137
48. Martin Y, Wickramasinghe HK (1987) Appl Phys Lett 50:1455
49. Saenz JJ, Garcıa N, Grutter P, Meyer E, Heinzelmann H, Wiesendanger R, Rosenthaler L, Hidber HR, Guntherodt H-J (1987) J Appl Phys 62:4293
50. Wittborn J, Rao KV, Nogues J, Schuller IK (2000) Appl Phys Lett 76:2931
51. Zhang L, Israel C, Biswas A, Greene RL, de Lozanne A (2002) Science 298:805
52. Chen Y, Ho S, Wuz T (2006) Electrochem Solid State Let 9:J27
53. Perry JM, Neville A, Hodgkiess T (2002) J Therm Spray Techn 11:536
54. Day HC, Allee DR (1993) Appl Phys Lett 62:2691
55. Garcia R, Martinez RV, Martinez J (2006) Chem Soc Rev 35:29