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The Working of the Atomic Force Microscope for Chemical Mapping

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Abstract: Since the invention of the scanning tunneling microscope (STM) in 1981 and the atomic force microscope (AFM) in 1986, over 5,000 publications have cited the article "Atomic Force Microscope" by G. Binnig, C.F. Quate, and C. Gerber (published in Physical Review Letters, 1986). This article presents a short review on the operating principle and possible applications of AFM with special attention devoted to chemical mapping. The article would be useful for beginners in AFM technique.

In 1959, Nobel Laureate Richard Feynman (Fig. **1**), from http://nobelprize.org/nobel_prizes/physics/laureates/1965/index.html) gave a lecture at a meeting of the American Physical Society where he talked about future opportunities for manipulating and controlling things on the very small scale – the nanoscale. It was the first time that the field of nanotechnology was posed to the world. In his talk, Feynman mentioned how in the year 2000 we might look back and wonder why it was not until the year 1960 that we began seriously to move into the field of nanotechnology. Ironically, nanotechnology eventually took off in the year 2000 because back in 1960, we simply did not have *the tools* to manipulate, control, or characterize things on the nanoscale. The invention of the scanning tunneling microscope (STM) and atomic force microscope (AFM) were major breakthroughs that opened the door to nanotechnology [1, 2].

Since the invention of the STM in 1981 and the AFM in 1986, over 5,000 publications have cited the article "Atomic Force Microscope" by G. Binnig, C.F. Quate, and C. Gerber (published in Physical Review Letters, 1986) [1,3]. And because of the continued research and development of these microscopes, together with their versatility, different surface types can be studied today by over 20 modified force microscopes, such as the magnetic force microscope (MFM), force modulation microscope (FMM), Kelvin probe force microscope (KPFM), electrostatic force microscope (EFM), and others. In this article, we aim to describe how chemical force microscopy (CFM) works and its application in providing chemical information of scanned surfaces.

INVENTION OF THE TOOLS

Gerd Binnig and Heinrich Rohrer developed a prototype of the STM in 1981 while working at the IBM Zurich Research Laboratory in Switzerland. They were later rewarded with the Nobel Prize in Physics in 1986 for the invention. (The prize was shared that year with Ernst Ruska for his design of the electron microscope. Fig. (**2**), from http://nobelprize.org/nobel_prizes/physics/laureates/1986/) Within a year of the invention of the STM, Binnig and coworkers used the microscope to resolve the structure of the Si(111)-(7x7) surface, one of the most intriguing unsolved problems in surface science at that time [4].

Fig. (1). Nobel Laureate Richard P. Feymann, (picture from http://nobelprize.org/nobel_prizes/physics/laureates/1965/index.html). His prize was shared with 3 other scientists for "their fundamental work in quantum electrodynamics, with deep-ploughing consequences for the physics of elementary particles".

Despite the success of the STM, it became evident that a similar scanning microscope which could be used for nonconducting surfaces would be more useful. The STM requires that the sample material be electrically conductive, because the microscope uses the tunneling current which flows between a biased tip and the sample. It reflects the strong distance-dependent probability of electron transport through a gap between two conducting solids. With careful observation early in the STM experiments, Binnig became aware of significant forces detected with the tunneling current when the tip-sample distance was small enough for a

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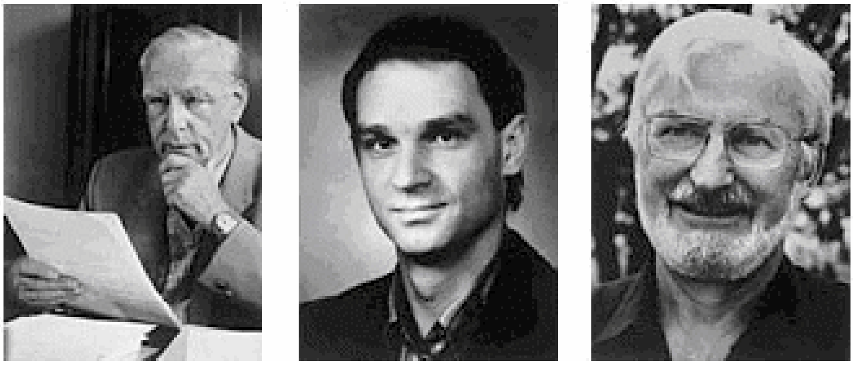

Fig. (2). Nobel Laureates Ernst Ruska, Gerd Binnig, and Heinrich Rohrer (left to right, picture from http://nobelprize.org/nobel_prizes/physics/laureates/1986/index.html). Ernst Ruska earned the prize for his fundamental work in electron optics, and for the design of the first electron microscope. Gerd Binnig and Heinrich Rohrer earned their prize for their design of the scanning tunneling microscope.

current to flow. In 1986 (while Gerd Binnig spent a sabbatical at Stanford with Calvin Quate and Christoph Gerber was at the IBM Research Laboratory in Almaden, California), they soon introduced a working prototype of the AFM [2, 5]. The forces were based on the short-range van der Waals interaction when the tip-sample distance was small (see Fig. (**3**), [3]). Because no electron transport is involved, both insulators and biological samples can be investigated down to atomic resolution. Information on topography [6-11], roughness [9, 10], friction [8], adhesion [8, 11], elastic properties [12, 13], magnetic field [14, 15], resistivity [16, 17], etc. can be obtained by the AFM with nanometer resolution.

PRINCIPLES OF ATOMIC FORCE MICROSCOPY

Binnig described the AFM as being much like the stylus profilometer, in that both are used to scan the surface, sense the variations of the sample, and generate three-dimensional images [3]. The AFM consists of a probe with a very sharp tip that is attached to a cantilever. Today, probes are mass fabricated by the microlithography process, much like

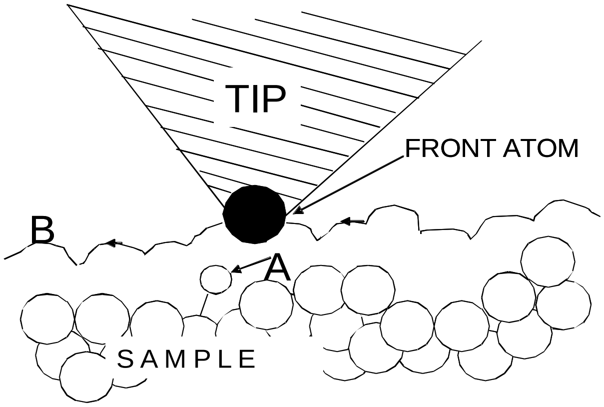

Fig. (3). Diagram of the short-range interaction force between the tip of the AFM (or STM) when in close contact with the sample surface [3].

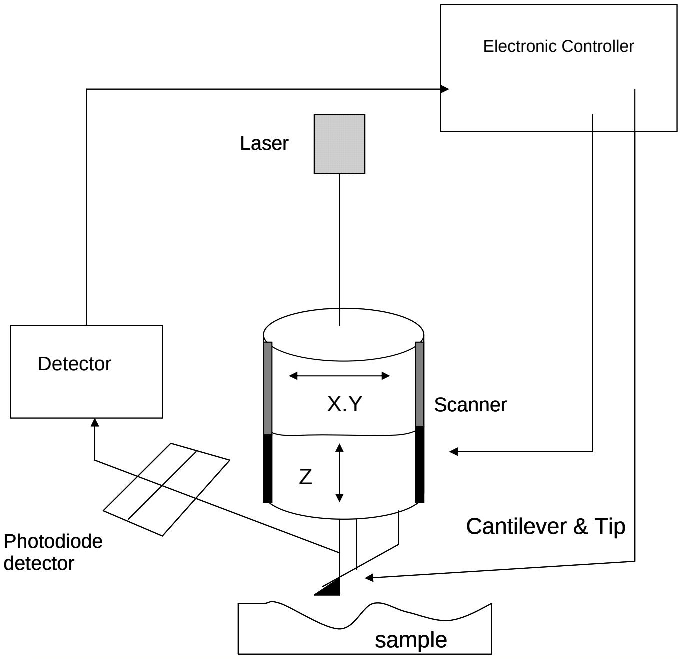

Fig. (4). Schematic diagram of the atomic force microscope.

computer chips. Probes are typically made of silicon or silicon nitride with a tip radius of curvature on the order of 5-20 nm. When the probe is scanned on the sample surface, the interaction between the tip and the atom on the surface of the sample causes the cantilever to bend as a result of van der Waals forces and other chemical bonds and forces. Forces on the probe can be either attractive or repulsive, depending on the nature of the interaction between the tip and the surface being investigated. The bending or deflection of the cantilever is in accordance to Hooke's law. The deflection of the cantilever is detected by a laser beam that is shined on the back of the cantilever and reflected onto a photodiode or a laser detector and processed by computer (Fig. **4**). Aside from the signal from the photodiode, another important signal comes from the piezoelectric tube where the sample is placed. The translation of the piezoelectric tube height is controlled by a feedback loop, which can maintain either a constant force or a constant distance between the tip and sample. Signals from both the photodiode and the piezoelectric tube are analyzed by computer software and a 3-dimensional image of the surface is reconstructed.

CHEMICAL MAPPING

Surface interfacial properties can play an important role in governing many of the initial reactions that occur in biological systems, biomedical materials, drug delivery systems, materials science, chemical reactions, and many other areas. While there are several techniques that allow us to study the chemical spatial distribution of these surfaces, none are able characterize the surfaces in their natural environment on the nanometer length scale [18-23]. Chemical force microscopy (CFM) is a branch of the AFM where the probe is chemically modified or functionalized [24]. Characterization can be done in the natural environment of the system, as the AFM does not require a special vacuum to operate. The CFM is an applied concept of lateral force microscopy (LFM) and is also known as frictional force microscopy (FFM). It is called LFM or FFM because it measures the lateral twisting of the cantilever as a result of molecular friction (Fig. **5**). Generally in the AFM, samples are scanned parallel to the direction of the cantilever setting which causes the up and down deflection of the cantilever (Fig. **6a**). In LFM, the sample is scanned perpendicular to the direction of the cantilever setting in which the molecular friction causes a lateral twisting of the cantilever (Fig. **6b**). A functionalized probe exhibits higher interaction (*molecular frictional interaction*) with specific domains on the specimen surface [25-31].

To detect a probe-specimen chemical interaction, three images of the same area are collected, namely the topography image, the lateral force (LF)-trace image, and the LF-retrace image. A topography image is often collected as a comparison to give information with regard to the z-axis and also to determine the similarity of the scanned area and quality. LF-trace and LF-retrace images are collected in opposite scanned directions. A post-image processing, trace-minus-retrace (TMR), is performed on the LF-trace and LF-retrace images to eliminate the height differences of the scanned area. Fig. (**7**) shows a diagram of how doing the TMR can cancel out the height differences and put forth only chemical interaction information. However, TMR will not be able to cancel out large height differences. Fig. (**8**) shows the topography image of an acid-treated starch granule, and the TMR image after image subtraction that draws out the specific chemical domain's interaction between the tip and the specimen surface [29].

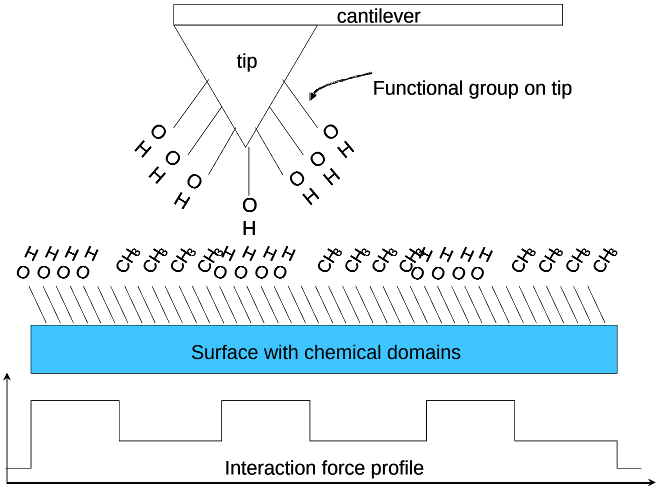

Fig. (5). Diagram of molecular friction interaction between a chemically modified probe and the surfaces of specific chemical domains.

APPLICATIONS

In 1994, Frisbie and co-workers first presented the working concept of the CFM in *Science* [32], where they focused on the adhesive and friction force measurement of organic monolayers of distinct functional groups. By using probe tips that have been functionalized with either hydrophobic (CH_3) or hydrophilic (COOH) molecules, they showed that the adhesive interactions between simple hydrophobic-hydrophobic, hydrophobic-hydrophilic, and hydrophilic-hydrophilic molecules can be measured.

Since Frisbie *et al.*'s work, there have been continuous applications of the CFM in various biological systems and materials science to understand the chemical spatial distribution of different surfaces and their functions. Schönherr *et al.* had used the CFM to study the inhomogeneous forces that was related to the variations of local 'pK_a' values and different local hydrophobicity that result from the inhomogeneous distribution of the polar functional groups on the polymer surface [33].

Specificity of the receptor–ligand pair of cell membranes has also been used as CFM. Grandbois *et al.* had shown affinity contrast imaging of group A and O red blood cells with the CFM [34]. It would be impossible to mention all the work conducted *via* the CFM, but the work in this area is well acknowledged by the research community. Examples include work by Raghavan *et al.* [35], Nguyen *et al.* [36], Sugimoto *et al.* [37], Termnak *et al.* [27], Wuttisela *et al.* [29], and Hansma *et al.* [38] are few to mention.

CONCLUDING REMARKS

Chemical force microscopy allows investigators to measure molecular forces and the chemical properties of surfaces. A detailed understanding of chemical spatial distribution and the morphology of surface structures is of

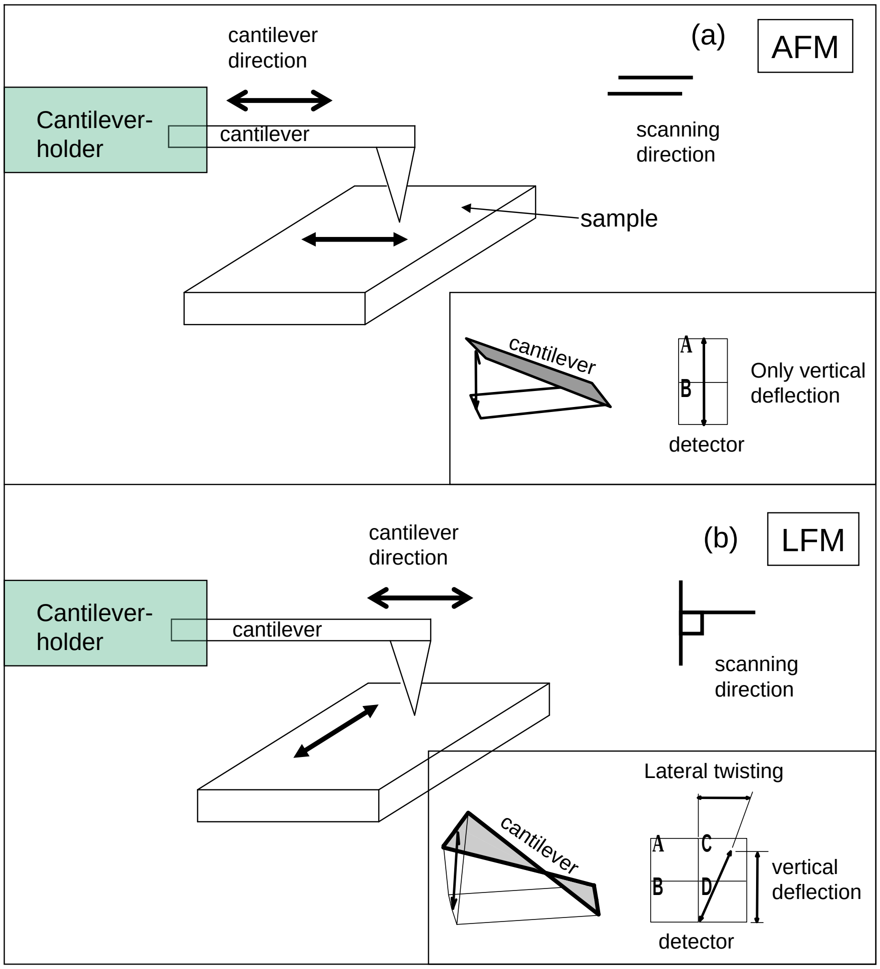

Fig. (6). Diagram to indicate the scanning direction of the cantilever. (**a**) Scanning parallel to the direction to which the cantilever is held by the cantilever holder results in only the vertical deflection of the cantilever in *AFM*; (**b**) Lateral twisting of the cantilever results from molecular friction and the scanning of the sample 90° to the direction in which the cantilever is held by the cantilever holder in *LFM*.

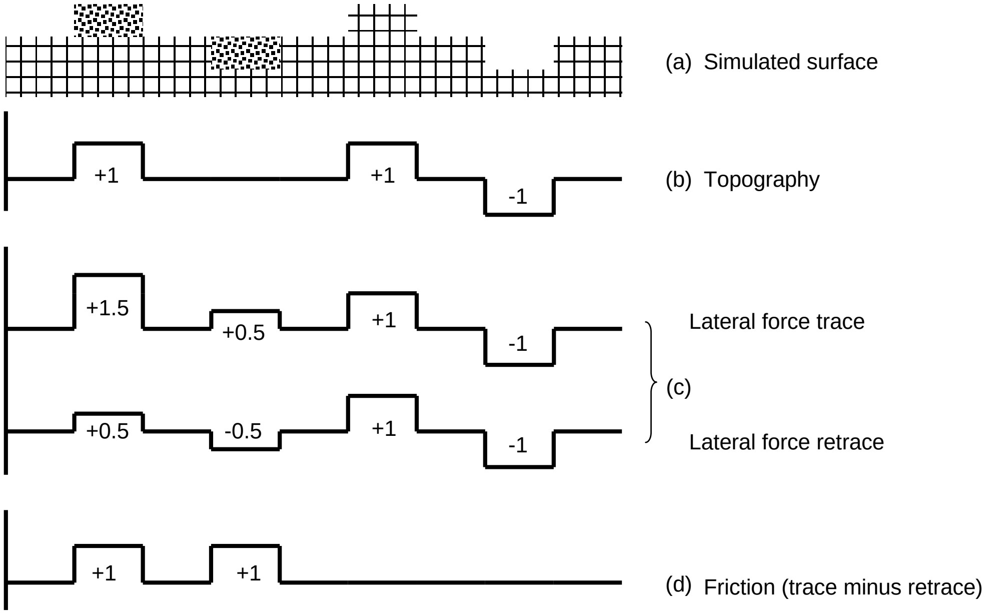

Fig. (7). Data processing concept of trace-minus-retrace (TMR). (**a**) Simulated surface with two types of materials having different chemical domains and areas with only height differences. (**b**) Topography profile of the simulated surface. (**c**) Lateral force (trace) and (retrace) profile, where both chemical domains and height information are coupled together, and lateral force (trace) and (retrace) information have opposite signs. (**d**) Result of trace minus retrace profile, leaving only the chemical domain information.

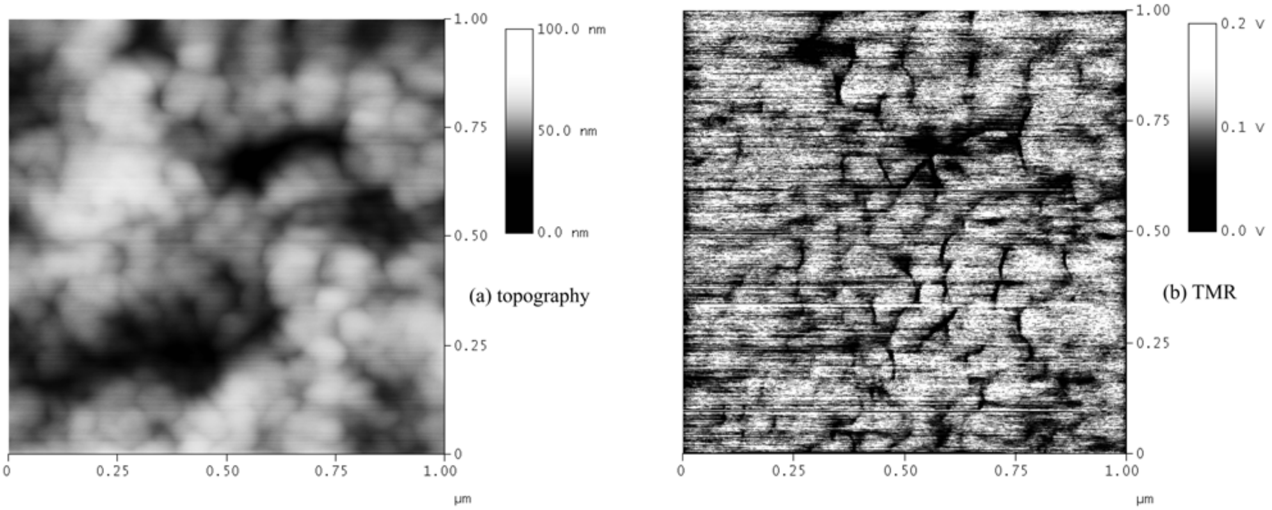

Fig. (8). (**a**) Topography image of a hydrolyzed starch granule using –OH probe. (**b**) TMR image that brings out a distinct chemical domain.

great importance, as it may govern the processes of many reactions that occur both in the bulk properties and on the nanoscale. It is most important to understand the nature of the surface being investigated to correctly interpret the interaction between the tip and sample.

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