

INTERFACE SCIENCE AND TECHNOLOGY

Advanced Chemistry of Monolayers at Interfaces

TRENDS IN METHODOLOGY
AND TECHNOLOGY

Toyoko Imae
Editor



Advanced Chemistry of Monolayers at Interfaces

Trends in Methodology and Technology

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INTERFACE SCIENCE AND TECHNOLOGY—VOLUME 14

Advanced Chemistry of Monolayers at Interfaces

Trends in Methodology and Technology

Edited by

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Preface

The monolayer science started from the investigation of adsorption monolayers on water and solid surfaces, which was developed by scientists as represented by Gibbs and Langmuir. The early researches were based on thermodynamics, and two-dimensional (surface) thermodynamic theories were established. The monolayer investigation furthermore evolved into Langmuir and Langmuir–Blodgett monolayers, which are an insoluble monolayer at air/water interface and its transfer film on solid substrate, respectively, and later into self-assembled monolayers. It should be noticed that the evolution of monolayer science involves intensively the development of methodologies in surface science, which made it possible to obtain the information at nano-scale level. The pioneering technique is a scanning probe microscopy, which enabled molecular ordering to visualize at an atomic scale. Secondly, the development of surface spectroscopy was enhanced by taking advantage of surface plasmon resonance phenomenon and allowed the highly supersensitive detection of molecular species at interface. Nanotechnology, that is, technology at nano-scale was developed in the last part of the 20th century, and it is one of key sciences in the 21st century. In this way the nanotechnology is supported by the development of monolayer science and surface methodologies.

This book describes the advanced chemistry of monolayers at interfaces. Especially the recent trends of methodology and technology are focused upon. The book introduces the methodologies of scanning probe microscopy, surface force instrumentation, surface spectroscopy, surface plasmon optics, reflectometry, and near-field scanning optical microscopy. The modern interface reaction method and the lithographic technology are also included. Such methodologies and technologies are indispensable in supersensitive and nano-scale sciences such as monolayer science. Those are applied to monolayers of surfactants, amphiphiles, polymers, dendrimers, enzymes, and proteins, which serve many uses. The researches range in different types of monolayers like adsorption, Langmuir, Langmuir–Blodgett, and self-assembled monolayers at air/liquid, liquid/liquid, liquid/solid, and air/solid interfaces. Recent monolayer chemistry runs on experiment, theory, and simulation at static and dynamic viewpoints, extends to analyses at not only steady state but also time-resolved state, and takes in bottom-up and top-down techniques. This book covers such research fields and regions. The book aims at contributing to the further development in research of academic and professional researchers, to the further knowledge of the students and to the further technological advancement in engineers' specialized field.

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Chapter 1

Scanning Tunneling Microscopy for Self-Assembled Monolayers

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1. INTRODUCTION FOR SCANNING TUNNELING MICROSCOPY

1.1. Principle

Among all the different types of surface imaging techniques, the scanning tunneling microscope (STM) presents the best spatial resolution and versatility. In fact, atoms and molecules can be literally touched one by one, thus opening new ways for investigating them [1]. The first and most amazing ability of the STM is to provide three-dimensional images of individual molecules and their environment at the atomic level. However, many other experiments can be conducted with an STM, as for instance manipulating particles, performing local spectroscopy, and even chemically modifying the sample. In a sense, STM has made it possible to act directly on atoms and molecules for the first time. This is the ultimate step of spatial resolution for chemistry, like femtosecond techniques are the ultimate step of time resolution for chemical reactions [2].

The basic principle of scanning tunneling microscopy (STM) is based on the tunneling current between a metallic tip, which is sharpened to a single atom point, and a conducting material (Fig. 1). A small bias voltage (mV to V) is applied between an atomically sharp tip and the sample.

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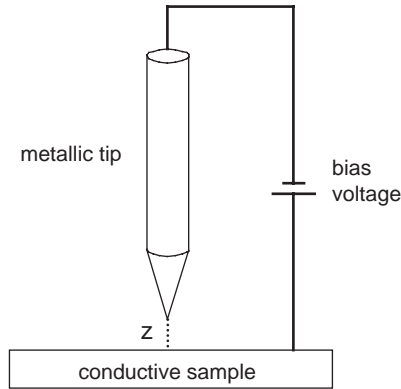


Fig. 1. Basic principle of the scanning tunneling microscopy technique.

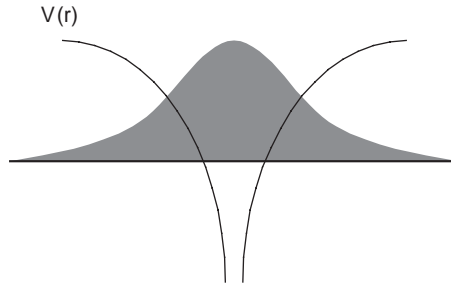


Fig. 2. Wave function of a valence electron in the Coulomb potential well $V(r)$.

If z , the distance between the tip and the sample, is large, no current flows. However, when the tip is brought very close ($< 10 \text{ \AA}$) without physical contact, a current (pA to nA) flows across the gap between the tip and the sample. Such current, which is called tunneling current, is the result of the overlapping wave functions between the tip atom and surface atoms. Electrons can tunnel across the vacuum barrier separating the tip and sample in the presence of a small bias voltage. The magnitude of the tunneling current is extremely sensitive to the gap distance between the tip and the sample. As we measure the current with the tip moving across the surface, atomic information of the surface can be mapped out.

To understand how STM works, it is vital to know what is tunneling current, and how it is related to all the experimental observations. Tunneling current is originated from the wavelike properties of particles (electrons, in this case) in quantum mechanics. When an electron is incident upon a vacuum barrier with potential energy larger than the kinetic energy of the electron, there is still a non-zero probability that it may traverse the forbidden region and reappear on the other side of the barrier. It is shown by the leak out electron wave function in Fig. 2.

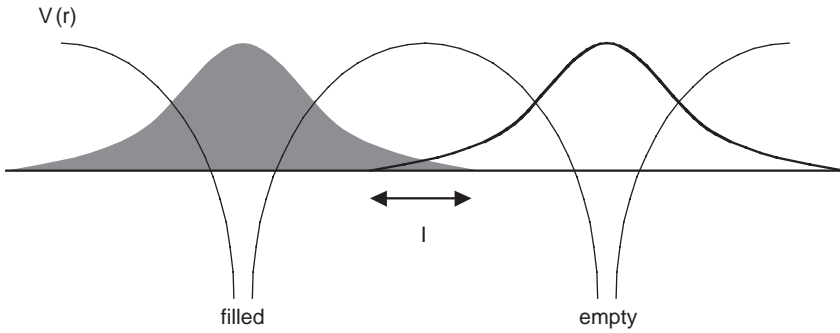


Fig. 3. Tunneling current I through vacuum between two atoms.

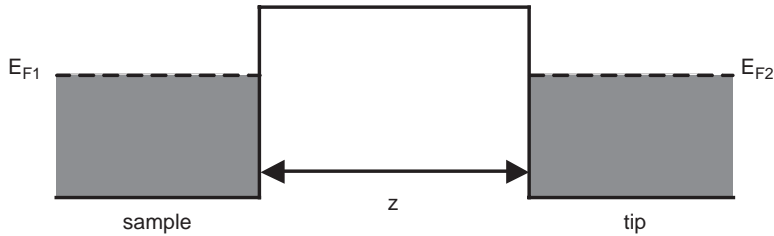


Fig. 4. Energy levels in two metals separated by a vacuum barrier.

If two conductors are so close that their leak out electron wave functions overlap, then an electron can tunnel back and forth through the vacuum or potential barrier between them, generating a tunneling current (Fig. 3).

In a metal, the potential barriers between the atoms in the interior are quenched and electrons move freely in the conduction bands. In other words, electrons exist within an energy range, designated by the shaded areas in Fig. 4, up to the respective Fermi levels, E_{F1} and E_{F2} . If an insulator, or indeed a vacuum, is inserted between two metals, an energy barrier appears. In our STM scheme, the thickness of the barrier corresponds to the tip-sample gap, z .

When a small voltage V is applied between the tip and the sample, the shape of the energy barrier changes. A difference between the Fermi levels E_{F1} and E_{F2} creates empty states on the right, generating a driving force for the electrons to tunnel across the barrier from the left side (Fig. 5).

Quantum mechanics allows a few electrons to traverse the barrier if the thickness z is small. The probability that an electron will cross the barrier is the tunneling current (I) flowing across the vacuum gap, and it decays exponentially with the barrier width z as

$$I \propto e^{-2Kz} \quad (1)$$

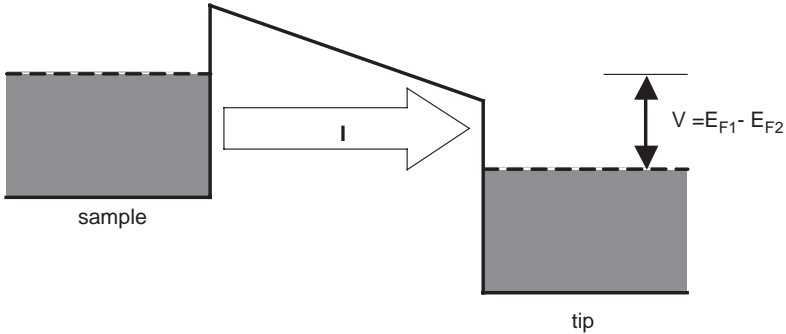


Fig. 5. Tunneling current I through vacuum when a bias voltage V is applied.

where z is the distance between tip and sample. K , which is the inverse decay length of the electronic wave functions at the Fermi level, is given by

$$K = \frac{\sqrt{2m(V - E)}}{h} \quad (2)$$

where m is the mass of the electron, E the energy of the state, V the potential in the barrier and h the Planck's constant. As a consequence, very small changes in the tip-sample separation induce large changes in the tunneling current. Therefore, the sensitivity to vertical distance is extremely high. Moreover, the tunneling current is only carried by the outermost tip atom: the atoms that are second nearest carry only a negligible amount of the current. In other words, the sample surface is scanned by a single atom only.

1.2. Apparatus

In order to obtain an image of the surface of the sample, the STM tip slowly scans across the surface at a distance of only an atom's diameter. This is represented in Fig. 6.

Two different modes of imaging have been developed: the constant current mode and the constant height mode. In the first experiment, the tip is scanned across the surface at constant tunnel current I_T , maintained at a pre-set value by continuously adjusting the vertical tip position with the feedback voltage V_z . In the case of an electronically homogeneous surface, constant current essentially means constant tip-sample distance z (Fig. 7).

On the other side, on surface portions with small unevenness, the tip can be rapidly scanned at constant z -position. Such "current images" allow much faster scanning than in the constant current mode, but a separate calibration of current/height is required. This mode is presented in Fig. 8.

The tip is moved across the surface by using a piezoelectric element. A voltage applied to two electrodes contracts the piezoelectric material in between, and the typical total excursion of a piezo is usually in the range of

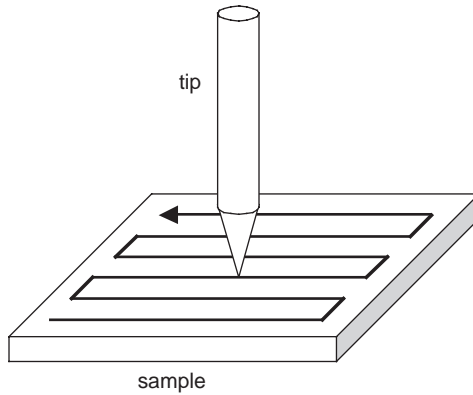


Fig. 6. The STM tip scans the sample surface in order to create an image.

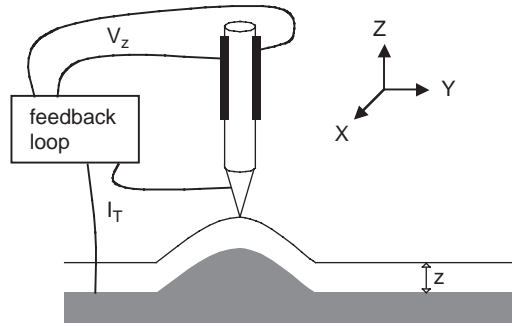


Fig. 7. Constant current mode of imaging with STM.

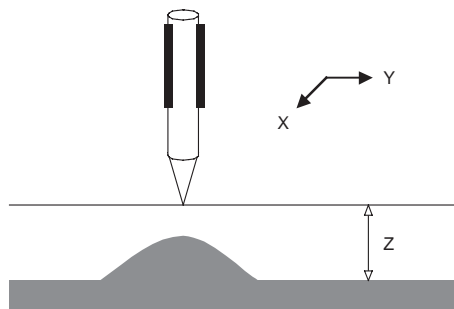


Fig. 8. Constant height mode of imaging with STM.

micrometers. Originally, the STM tip was mounted on a three-part piezo element (Fig. 9), with three different piezo bars used to move the tip in all the three dimensions of space.

However, nowadays a piezo tube is more commonly used. In this geometry, the inner and outer surfaces of a tube of piezoelectric material are coated with

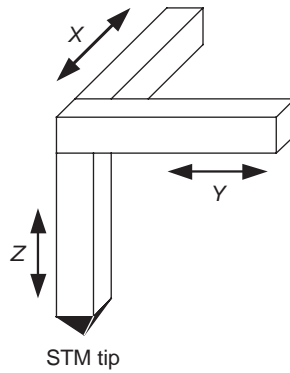


Fig. 9. STM tip mounted on a three-parts piezo element.

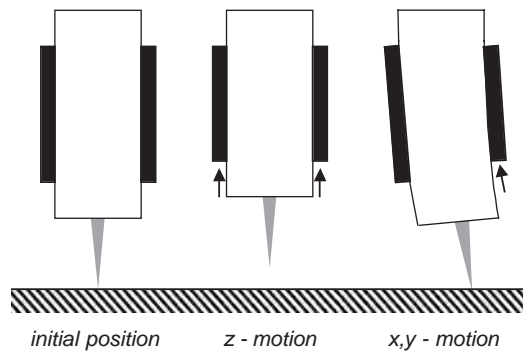


Fig. 10. Principle of operation of a piezo tube.

a thin metal electrode. The outside is separated into four sections, which are electrically isolated from each other. For the lateral motion of scanning, the voltage is applied across the tube, while for the vertical motion, the voltage is applied between the inside and the outside of the tube (Fig. 10).

Different metals and different processes can be used to prepare the tips. Mechanically cleaved platinum/iridium tips (4:1) provide very sharp atomically resolved images, and furthermore they are cheap, easy to prepare, and stable. However, the exact shape of the tip differs from one experiment to another: the high resolution is achieved by randomly created minitips of potentially atomic size rather than by a perfect cone decreasing to a single atom end. In addition, the general shape of the tip is not conical, which can be necessary in some optical setups for coupling with spectroscopy. Therefore, a lot of effort has been done to produce reproducible electrochemically etched tips. The basic setup is depicted in Fig. 11.

Some papers on how to prepare Pt/Ir tips have been published, with end curvature of the tip smaller than 100 nm [3]. Tungsten tips are somehow easier to fabricate, and tip radius of about 20 nm have been reported [4–6]. Silver tips

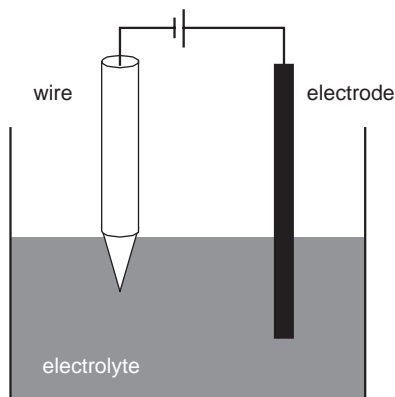


Fig. 11. Basic scheme to prepare tips by electrochemical etching.

can also be obtained [7–9], but silver is not very stable under ambient conditions because of oxidation. Finally, gold tips can be difficult to work with, mainly due to the inherent softness of the metal [10].

1.3. Sample Preparation

Organic molecules with long alkyl chains are known to form monolayers on definite solid surfaces by self-adsorption. Highly oriented pyrolytic graphite (HOPG), which presents an atomically flat surface that can be cleaned mechanically, is the substrate of choice. However, in some spectroscopic experiments using an inverse microscope for instance, a transparent sample is required. In these cases, a quartz glass substrate covered by a thin layer of indium tin oxide (ITO, ~ 100 nm) can be used. The surface is not as flat as with HOPG, but the sample is transparent and conductive, an obvious requirement for STM. Typical self-adsorbed molecules are stearic acid, dioctadecyl ether, and dioctadecyl selenide dissolved in 1-phenyloctane.

After preparing the surface of HOPG by cleaving one layer of graphite, the substrate is installed onto the piezoelectric scanner of the STM head. Subsequently, a few microliters of solution are deposited on the substrate with a micropipette, immediately forming a physisorbed monolayer. A freshly cleaved tip is then manually approached to the surface at a distance of about 0.5 mm, and the feedback mechanism is turned on. The automatic approaching mechanism brings the tip to a very close distance above the monolayer, namely about 1 nm, with the end of the tip into the solution drop. Fig. 12 presents the experimental setup for imaging this kind of monolayer at the solid–liquid interface. Note that the tip is immersed in the supernatant solution during scanning.

The main advantage of this solid–liquid setup is that the experiment can be carried out in air, which is normally unstable due to the condensation of water on the tip and/or onto the sample. Water is highly conductive, and since the