GUIDELINES FOR STUDENTS PREPARATION

Testing nanomaterials with scanning probe microscopy

Abstract

The lab provides the training students to use a scanning probe microscopy (SPM) (NANOEDUCATOR) for studying structure of the nanomaterials surface. After the finishing labs students know the background, features, application and facility of SPM. Particularly, they are able to prepare the sample and etch the probe tip for surface scanning, to get the image of the surface under different modes: scanning tunnel microscopy and atomic force microscopy, to process the image after scanning, and to draw the report of carried out work in English.

Time for implementing – 4 (four) hours).
USED TERMS

to develop nanotechnologies – развивать нанотехнологии
nanoceramics – керамические наноматериалы
surface structure (surface morphology) – морфология поверхности
surface property – свойство поверхности
sample (specimen) – образец
to smooth (polish) the surface – отшлифовать поверхность
scanning probe microscopy – сканирующая зондовая микроскопия
scanning tunneling microscopy – сканирующая туннельная микроскопия
atomic force microscopy – атомно-силовая микроскопия

to switch on the computer – включить компьютер
to switch off the computer – выключить компьютер
to download the program – загрузить программу
to copy a file – скопировать файл
to save a file – сохранить файл

probe (tester)– зондовый датчик
tungsten wire – вольфрамовая проволока
electrolysis device – прибор для электролиза
measuring head – измерительная головка

forward speed of scanning – скорость сканирования вперед
backward speed of the probe – скорость возвращения зонда
feedback – обратная связь
feedback amplification – усиление обратной связи
efficiency – добротность
frequency amplitude – амплитуда частоты
lid with camera – крышка с встроенной камерой

electrochemical etching – электрохимическое травление
to cut the wire off – отрезать проволоку
to straighten the wire – выпрямить проволоку
to turn the tip down – загнуть конец (проволоки)
thin film – тонкая пленка
to etch the wire – травить зонд
to pull the wire – протянуть проволоку
to drop on the floor – уронить на пол
to lay the sheet of white paper — подложить кусок белой бумаги под
funnel — воронка
to wind up the wire — смотать проволоку
to lower — опустить
to lift up (raise) — поднять
to take the alkali’s mass — взвесить щелочь
to use scales — использовать весы
to fix with a bolt — закрепить болтом
to insert — вставить (например, образец)
to paste — вставить (информацию в Word)
to be sure it’s fixed — удостовериться, что все закреплено
to bend on ninety degrees — согнуть на 90°
to bend a small tip down — загнуть маленький кончик
to insert in the hole of the tube — вставить в полость трубки
to take smth with pincers — взять что-то пинцетом
measuring cylinder — мерный цилиндр
distilled water — дистиллированная вода
to stir until total dissolution — взболтать до полного растворения
to push (insert) the probe — вставить зонд

experimental data — экспериментальные данные
image processing — обработка изображения

to choose the conditions — выбрать условия
to scan the surface — сканировать поверхность
to find resonance — найти резонанс
to fix the sample — закрепить образец
to stick the sample — приклеить образец
to be careful (gentle) — быть осторожным (деликатным)
to supply the probe to the surface — подвести к поверхности зонд
to get the probe away from the surface — отвести от поверхности
to find out — выяснить (причину)
scanning mode — режим сканирования
to figure out the features — разглядеть особенности
resolution and accuracy — разрешение и точность
INTRODUCTION

Scanning Probe Microscopy (SPM) is a branch of microscopy that forms images of surfaces using a physical probe that scans the sample. An image of the surface is obtained by mechanically moving the probe in a raster scan of the sample, line by line, and recording the probe-surface interaction as a function of position. SPM was founded with the invention of the scanning tunneling microscope in 1981.

The scanning tunneling microscopy is proposed as a method to measure forces as small as $10^{-18}$ N. As one application for this concept, we introduce a new type of microscope capable of investigating surfaces of materials on an atomic scale. The atomic force microscope is a combination of the principles of the scanning tunneling microscope and the stylus profilometer. It incorporates a probe that does not damage the surface.

Many scanning probe microscopes can image several interactions simultaneously. The manner of using these interactions to obtain an image is generally called a mode.

The resolution varies somewhat from technique to technique, but some probe techniques reach a rather impressive atomic resolution. They owe this largely to the ability of piezoelectric actuators to execute motions with a precision and accuracy at the atomic level or better on electronic command. One could rightly call this family of technique 'piezoelectric techniques'. The other common denominator is that the data are typically obtained as a two-dimensional grid of data points, visualized in false color as a computer image.

Advantages of scanning probe microscopy

- The resolution of the microscopes is not limited by diffraction, but only by the size of the probe-sample interaction volume (i.e., point spread function), which can be as small as a few picometres. Hence the ability to measure small local differences in object height (like that of 135 picometre steps on $<100>$ silicon) is unparalleled. Laterally the probe-sample interaction extends only across the tip atom or atoms involved in the interaction.
- The interaction can be used to modify the sample to create small structures (nanolithography).
- Unlike electron microscope methods, specimens do not require a partial vacuum but can be observed in air at standard temperature and pressure or while submerged in a liquid reaction vessel.
Disadvantages of scanning probe microscopy

- The detailed shape of the scanning tip is sometimes difficult to determine. Its effect on the resulting data is particularly noticeable if the specimen varies greatly in height over lateral distances of 10 nm or less.
- The scanning techniques are generally slower in acquiring images, due to the scanning process. As a result, efforts are being made to greatly improve the scanning rate. Like all scanning techniques, the embedding of spatial information into a time sequence opens the door to uncertainties in metrology, say of lateral spacing and angles, which arise due to time-domain effects like specimen drift, feedback loop oscillation, and mechanical vibration.
- The maximum image size is generally smaller.
- Scanning probe microscopy is often not useful for examining buried solid-solid or liquid-liquid interfaces.

General Principles

The scanning tunneling microscope (STM) was invented by G. Binnig and H. Rohrer in 1982 and they were subsequently awarded the Nobel Prize for Physics in 1986. From an experimental standpoint, the basic idea is as follows: a fine metal tip is brought close to a surface (typically to within one nanometer) and the current flowing between tip and surface is measured when a voltage is applied across the gap. According to classical physics, as there is no contact between the tip and the surface, no current can flow (open circuit). But according to quantum mechanics, if the distance between two electrodes (here, the tip and surface) is small enough, a current can in fact flow across the gap between the tip and the surface. This is the so-called tunnel effect, which has given its name to the microscope based upon it.

The tunnel effect, a purely quantum phenomenon, was first hypothesised in 1927. A particle such as the electron, described by its wave function, has a nonzero probability of penetrating a barrier, although this would be forbidden in classical mechanics. As a consequence, the electron can actually cross a barrier which separates two classically allowed regions. The tunneling probability, i.e., the probability that an electron will pass from one electrode to the other across the barrier, decreases exponentially with the width of the barrier. The tunnel effect can therefore only be observed for narrow barriers, of the order of the nanometer. Theory shows that the current detected is related to the chemical nature of the opposing surfaces, and this on the atomic scale. The microscope is based on a combination of two factors: controlled approach of a metal tip towards a conducting surface, using
piezoelectric tubes, and a high-performance anti-vibration system. The piezoelectric tubes have extension coefficients of the order of a few Å/volt and can thus ensure very accurate movements of the tip (bonded onto a piezoelectric ceramic) relative to the fixed surface by applying very low voltages (a few volts).

**Programs**

There are several programs used for image data analysis:

- **FemtoScan Online** - Software for SPM images processing.
- **GXSM** - Gnome X Scanning Microscopy.
- **Mountains-SPM** - Image processing and analysis from Digital Surf.
- **SPIP** - Scanning Probe Image Processor.
- **WSxM** - freeware for Scanning Probe Microscopy images analysis and representation
- **XPMPro** - Data acquisition, image processing and analysis from RHK Technology, Inc.

**LAB 1. PREPARATION OF TUNGSTEN PROBE TIP**

**Aim**: to shape the tip of the tungsten wire by electrolysis before scanning surface with SPM.

**Introduction**

Probe tips are normally made of platinum/iridium or gold. There are two main methods for obtaining a sharp probe tip, acid etching and cutting. The first involves dipping a wire end first into an acid bath and waiting until it has etched through the wire and the lower part drops away. The remainder is then removed and the resulting tip is often one atom in diameter. An alternative and much quicker method is to take a thin wire and cut it with a pair of scissors or a scalpel. Testing the tip produced via this method on a sample with a known profile will indicate whether the tip is good or not and a single sharp point is achieved roughly 50% of the time. It is not uncommon for this method to result in a tip with more than one peak; one can easily recognize this scan due to a high level of ghost images.

**General information about probes**
In SPM, a probe is raster-scanned across an object. The first high-resolution scanning probe microscope has been developed by Crewe in the late sixties, and his group built a scanning transmission electron microscope (STEM), which attained atomic scale resolution. This was achieved by using a cold field-emitter based on an etched single crystal tungsten wire that produced electrons emerging from a 100 Å spot. A single lens demagnifying this spot 50x and double deflection scan coils produced exciting images of biological macromolecules that fostered the development of multiple STEMs around the world. This type of instrument allows the mass of single macromolecules to be determined and images of unprecedented clarity to be acquired – possibilities of great potential for biological studies. However, only few STEMs are currently operated for biological applications.

Etched tungsten wires were also key to the scanning tunneling microscope (STM) built by Binnig and Rohrer in the eighties. The tip is simply brought so close to a conducting surface that electron tunneling between tip and sample occurs. The steep dependence of tunneling current versus tip-sample distance allowed surfaces to be contoured at atomic scale resolution. The STM was yet another novel instrument that was applied in biology, and that spurred the hope of biologists and physicists to achieve such goals as direct reading of DNA sequences, just like the STEM did a decade before. But the breakthrough came with the invention of the atomic force microscopy (AFM), again by Binnig. In the AFM the deflection of a highly flexible cantilever to which the tip is attached is monitored while the tip is raster-scanned over the sample. By keeping this deflection constant, forces acting on the sample can be reduced to a level that prevents significant deformations of soft biological material. Importantly, this operation can be executed while the sample is submerged in a physiological salt solution and kept at room temperature. Biomacromolecules can thus be observed at work.

New avenues emerge for assessing not only the surface topography at high spatial resolution with the AFM but also the local electronic properties of single membrane proteins. Protein unfolding experiments can now be analyzed quantitatively and understood to the single amino acid level and provide indirect information on the 3D atomic structure of the addressed proteins and their interaction with ligands, adjacent proteins, and lipids. Recent advances in high resolution imaging of native membranes suggest exciting applications of AFM technology for the study of biological systems. This development fosters great expectations for future progress in assessing membrane proteins in their native environment by AFM, identifying specific proteins by their surface structure, and assessing their nanomechanical as well as electronic properties in situ.
Probe Tip Preparation

For measurements in air, tips are made from a platinum–iridium wire of diameter 100–250 µm. This is an alloy that does not oxidize in air, an essential point, since an oxide layer would insulate the tip and make measurements very difficult. To obtain a fine tip, the simplest method is to cut the wire whilst stretching it, with cutting pincers. One then obtains a stretched wire with tiny barbs or spurs that can be used as nanotips. A certain degree of dexterity is required to achieve a good tip. The advantage with this technique is that, even though it is rather random, it is very quick to implement.

In ultrahigh vacuum, the metal used is tungsten. Tips are prepared by an electrochemical process followed by refinement in ultrahigh vacuum. The tip is thus reshaped by electrolysis. This requires a solution of NaOH (1mole/l), a molybdenum counterelectrode, a micrometer screw which controls the length of immersed wire, an electronic device which provides a continuous or alternating voltage, and a system for detecting tip rupture. There are several stages in the process. First the oxide layer on the wire is removed by applying an alternating voltage of around 20V peak-to-peak. The wire is then immersed to a length of a few hundred microns and a continuous voltage of around 5V is applied. This stage generally lasts between 4 and 5min. The electrolyzing current just before rupture is between 150 and 600 µA.
LAB 2. SCANNING THE SAMPLE SURFACE

Aim: to obtain the surface image of given sample under the different modes: scanning tunnel microscopy and atomic force microscopy.

General setup of STM

The three piezoelectric tubes displace the tip in the three directions x, y, and z. A voltage V is applied between tip and surface. The current I is measured and compared with a reference value I0. The ‘error’ signal is sent into a feedback loop, converted into a voltage applied to the z piezotube. The z information reaches a PC where it is converted according to a color scale for display as an image. The x and y piezotubes are controlled by the PC in such a way as to scan the sample. If necessary, power amplifiers are used to increase the output voltage of the PC (generally of the order of ±10 volts) into the range ±200 volts so that an xy scan of several microns can be achieved.
Setup of NanoEducator

1 – base,  
2 – sample keeper,  
3 – interaction sensor,  
4 – screw for fixing of sensor,  
5 – screw of manual supply,  
6 – screws for sample moving,  
7 – protective cover with camera.

Figure. External appearance of measuring head:

Conditions of scanning

Scanning field $70 \times 70 \times 10 \mu m$ (10 %).  
Min step of the probe - 1 Å.  
number of points in the frame $1024 \times 1024$ (dynamic memory must be 64 Mb).  
Current range - 100 pA till 200 nA.

Probe parameters:

range of frequency resonance between 6 and 14 kHz (typically 8 kHz).  
radius of curvature 100 nm (till 10 nm).

Resolution and accuracy:

AFM: X-Y ~50 nm (it is up round radius of the probe tip), Z – 2 nm  
STM X-Y ~50 nm ((it is up round radius of the probe tip), Z – 2 nm

Progress of work

1) To fix the sample given by teacher to the measuring head of NANOEDUCATOR  
2) To fix the probe to the probe keeper of measuring head  
3) To tune the frequency resonance of the prepared probe.
4)

5) To supply the probe tip to the surface: firstly manually; secondly, with the help of Nanoeducator Program.

6) To carry out the scanning under given conditions

7) To transform the image to 3D vision
8) To describe the surface with the help of teacher.
9) To draw the report about carried out work.

Former:
As..profp., PhD, Anna Godymchuk
LABORATORY REPORT (SAMPLE)

1) The lab report is supposed to start from the title page, which is to have data about the place of carried out work, name of student and name of teacher with signatures.

2) On the following pages the students is to include the information:

Date (dd.mm.year)
Theme of the work
Short annotation of done work
General setup of SPM Nanoeducator with short description of the process
The progress of work (lab 1, lab 2)
The experimental data
Discussions
Reference
Conclusions

3) The work is considered to be finished when defended in English.