The investigation and fabrication of nanometer-scale structures becomes a reality due to the development of scanning tunneling microscopy and related techniques. The final goal, manipulations with the individual atoms and molecules, has been achieved. D.M. Eigler used the scanning tunneling microscope (working at low temperatures ca. 4 K) to position individual xenon atoms on a single-crystal nickel surface with atomic precision. Mesoscopic systems composed of metallic or non-metallic clusters are intensively studied because of their new and interesting properties, and perspectives of subsequent application in nanolithography in order to create various structures of a very high degree of miniaturization. In this review, (i) the potential of scanning probe microscopes for revealing subtle details of surfaces down to atomic resolution is presented, (ii) a variety of different atomic manipulations processes and other surface modifications are reviewed against the background of different, more or less universal approaches, and finally (iii) a few examples of cluster surface structures created and/or modified by means of scanning tunneling microscope are demonstrated.

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1. Introduction

The prospect of manipulating matter on the atomic scale has fascinated scientists for decades. Up to early 80-ies there was a lack of techniques enabling the observation of individual atoms in a real space, and the more so as there was no techniques enabling the manipulation of individual atoms or molecules. The breakpoint came with the invention of scanning tunneling microscope (STM) by Binnig and Rohrer et al. [1], and further development of the wide variety of related techniques. These techniques may be labelled as local probe methods (LPM) because most of them use a sharp tip with a radius of curvature of about a few nm to several tens of nm, as a probe placed in the close proximity of an object. LPM are based on the whole family of scanning probe microscopies (SPM). The wide variety of different SPM constructions is presented in a few books and compiled materials of STM conferences [2–4].

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Scanning probe microscopes were quickly used for the fabrication of nanometer-scale structures [5, 6]. Finally, D.M. Eigler has used the STM at low temperatures (4 K) and in ultra high vacuum (UHV) conditions to position individual xenon atoms on a single-crystal nickel surface with atomic precision [7]. This was an unprecedented experiment which proved the possibilities of SPM technique and at the same time the limits of the technique.

Mesoscopic systems composed of metallic or non-metallic clusters and/or molecules are also intensively studied because of their new and interesting properties and perspectives of subsequent application [8]. The surface structures composed of clusters are expected to be stable at room temperatures and they may find applications in nanolithography to create various structures of a very high degree of miniaturization. Many examples of regular arrays of clusters created and controlled by SPMs [9–11], as well as some examples of cluster arrays modifications, obtained by applying voltage pulses (between the tip probe and the sample) or induced by thermal treatment [12, 13] have been published.

2. Rise of local probe methods

The original goal of Binnig and Rohrer was to learn about the local structural, electronic and growth properties of very thin insulating layers. The term "local" meant on the scale of the inhomogeneities of those properties, which means, on a few nanometer scale, a scale that was entirely inaccessible with existing techniques. Figure 1 presents the original idea of the STM based on a piezoceramic tripod [14]. A conducting sample and a sharp metal tip, which acts as a local probe, are approached each other within a distance of a 1 nm order. There is a significant overlap of the electronic wave functions due to this proximity of the probe and the sample. With an applied bias voltage (in the range of 1 mV up to 4 V) a tunneling current of 1 nA order can flow from the occupied electronic states near Fermi levels of the one electrode into the occupied states of the other electrode. The piezodrives $P_x$ and $P_y$ scan the conducting tip over the surface. The control unit applies appropriate voltage to the piezodrive $P_z$ to keep tunnel

Fig. 1. Principle of operation of the STM. (Description in the text; distances and sizes not to scale).
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current constant at a constant tunnel voltage via elongation or contraction the \( P_z \) piezodrive. The broken line indicates the \( z \)-displacement in a scan over a surface step (A) and a chemical inhomogeneity (B). The exponential dependence of the tunneling current on the tip to sample spacing has proven to be the key for the high spatial resolution which can be achieved with STM

\[ I \propto \exp\left(-A\phi^{1/2}s\right), \]

where \( \phi \) is the mean local tunneling barrier height, \( s \) is the separation between the tip and the sample surface, and \( A \approx 1 \text{ Å} \left(\text{eV}\right)^{-1/2} \). Figure 2 shows the most typical STM images of highly oriented pyrolytic graphite (HOPG — Fig. 2A) and the \( 7 \times 7 \) reconstruction of Si(111) (Fig. 2B) surfaces obtained with the atomic resolution.

![Fig. 2. Atomic resolution STM images of (A) HOPG, 2 x 2 nm², (B) the 6 x 6 reconstruction of Si(111) surface.](image)

Atomic force microscope (AFM) was invented by Binnig and co-workers in 1986 year [15]. The AFM records interatomic forces between the apex of a tip and atoms in a sample as the tip is scanned over the surface of the sample. Figure 3A shows a schematic diagram of an AFM construction and operation principle. The essential features are a tip, shown as a rounded cone, a spring, and a spring deflection sensor. The spring deflection sensor is usually based on the deflection of a laser-light beam reflected off the back of the spring, however it can be also based on electron tunneling to the back of the spring. The small repulsive tracking forces between the tip and the sample, usually in the range of \( 10^{-6} \) to \( 10^{-9} \) N, are recorded by measuring minute deflections of the cantilever for which the typical spring constant would be about 1 N/m. All that is required, to obtain the image of the sample surface, is an electrical signal that varies rapidly with the deflection. This signal is sent to the same type of electronics used for STM. The concept of using a force to image a surface is a general one and can be applied to magnetic and electrostatic forces as well as to the interatomic interaction between the tip and the sample [16]. The possibility that the AFM can image nonconducting samples with an atomic resolution is one of the major differences and advantages over the STM. The first atomic resolution image of a nonconductor was obtained by
Albrecht et al. [17] on a boron nitride surface. Figure 3B shows another example — the AFM gray-scale image of mica obtained in air using “OMICRON” AFM showing hexagons of SiO$_4$ tetrahedra with a diameter of 0.55 nm.

STM and AFM are prototypes of different instruments, which were constructed for investigations of materials in a nanometer scale, e.g., electrochemical STM, photon STM, magnetic force microscope, etc. [2-4]. It is impossible to list all of them within this review.

3. Nanofabrication and atomic manipulations
the scanning probe microscopes

Every instrument that images the sample has to interact with its object. Only when the transferred energy or momentum is small enough that the sample is not permanently modified, it can be looked upon as a microscope in the proper sense. SPMs usually fulfill this requirement, however their configuration enables switching to a “modifying” mode by changing the experimental parameters (e.g., a bias voltage or AFM cantilever loading force). Originally, modifications of the sample happened accidentally and were visualised during STM inspection of the sample after a “modifying” event as it was done by Ringger et al. [5] on a glassy Pd$_8$Si$_{19}$ sample or by van Kempen et al. [6] on Au surfaces. More and more scientists have been using STM and AFM to modify surfaces in different ways, e.g., by local pinning of the molecules to a surface and by transfer of an atom from the STM tip to the surface. All these processes can be classified according to different schemes, and two of these schemes will be presented below.

3.1. An universal approach

An universal approach allows one a general discussion of the proper modifications process without the need to refer directly to a specific SPM. This clas-
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Sification is coming from Shedd and Russell [18] and originally was adopted for all so-called “nano-lithography” processes performed with one of SPMs. The idea of their scheme was that only three basic quantities can be responsible for the modification of a sample: (i) the energy flux into a sample; (ii) the potential barrier between the tip and the sample; (iii) the forces acting between the tip and the sample. The values of these basic quantities can be changed by two control parameters, the tunnel current and the electric field, which in turn depend on the bias voltage applied between the tip and the sample, and the width of the tunnel gap. Some authors [19] add the energy quantum as a fourth basic quantity, because some of desired reactions such as dissociation of a molecule might demand a well-defined quantum of energy supplied by the kinetic energy of an electron or by photon propagating in the gap between the probe and the sample.

Dransfeld and Xu [20] have studied different mechanisms involved in the heat transfer between the sample and the probe. They found that in UHV condition the heat transport by thermally excited electric fields is dominant, and finally may cause some local modifications on the surface. E.g. Staufer et al. [21] have used STM to modify glassy metals in UHV. By increasing the bias voltage from 0.1 V to 1.0 V and the current from 1 nA to several μA the authors have generated hillocks and line shape structures in the range of a few nm as the consequence of local melting of the surface.

A certain energy quantum may be demanded to induce a single event, either a decomposition of a molecule or a linkage of molecules, e.g., during the exposure of any conventional electron or photo-resist. In order to expose such a resist with an STM the bias voltage must be set close to or at the value where the field emission takes place.

Two types of forces are probably the most important for the modification of a surface: the contact forces and the electrostatic forces. The theoretical consideration about force interactions that are essential for force microscopy were done by Landman et al. [22]. They showed, using the Monte-Carlo simulations that, besides plastic and elastic deformations, transfer of atoms from the probe to the sample or vice versa may occur during contact formation.

The potential barrier between the probe and the sample is also of interest for atoms being transferred from or to the sample. The height of the barrier can be influenced either by the gap distance or by the electric field. Tunneling of atoms becomes important only if the gap distance is reduced to 0.01 nm. This process will be enhanced by thermal activation. Gomer [23] found that the strong electric fields (≈ 10¹⁰ V/m) may form a potential suitable for field desorption of an adsorbate or for field evaporation of an atom from the tip.

3.2. Parallel and perpendicular processes

This approach was introduced by Stroscio and Eigler [24]. They divided a variety of atomic manipulation processes into two classes: parallel and perpendicular processes. Parallel processes may be in turn divided into (i) field-assisted diffusion and (ii) sliding processes. In both, the bond between the manipulated atom and underlying surface is never broken.
(i) Due to proximity of the probe and the sample in STM (usually $\approx 0.5$ nm), and the bias polarization of 1 V to 10 V, the electric field strength is in the range of $(0.2$ to $2) \times 10^{10}$ V/m. The field is inhomogeneous and concentrated in the vicinity of the probe tip, as it is shown in Fig. 4 for a 10 nm radius tip positioned 0.5 nm above a metal surface with a 3 V potential difference. The interaction of the spatially inhomogeneous electric field with the dipole moment of an adsorbed atom leads to the potential energy gradient, or force along the surface, which results in a field-assisted directional diffusion of the adatom. This effect was demonstrated by Whitman et al. [25] with Cs atoms on GaAs and InSb surfaces. This process is shown in Figs. 5A–F. The directional diffusion was discussed by Stroscio et al. [24] in terms of the potential energy gradient of an atom in an electric field. The spatially dependent energy of the atom is given by a formula

$$U(r) = -\mu \cdot E(r) - \frac{1}{2} \alpha \cdot E(r) + \ldots,$$

(2)

where $\mu$ is the static dipole moment, $\alpha \cdot E$ is the induced moment, $\alpha$ is the polarizability tensor. This potential energy is added to the periodic surface potential as it is presented in Fig. 6A. The interaction of the electric field with the adsorbate dipole moment gives rise to a broad potential well where an atom would feel a force to move it to the bottom of the well under the apex of the tip.

(ii) The magnitude and the direction of the force exerted on the adsorbate by the tip may be controlled by changing the distance between the adsorbate and the tip, e.g. by increasing the tunnel current keeping the bias polarization constant. In such a case, an attraction of an adsorbate to the tip by a chemical binding force gives rise to a potential well located directly below the tip (Fig. 6B).
adsorbate would remain trapped in the well during a lateral tip movement, as it is depicted in Fig. 6C. The ability to manipulate individual atoms was demonstrated in this way for the first time by Eigler et al. [7], who used this idea to position Xe atoms on a Ni(110) surface. The famous "IBM" mark symbol was composed of 35Xe atoms just using this method. However it should be pointed out that this procedure was performed in ultra high vacuum (UHV) and at low ($\approx 4$ K) temperatures. It was necessary to keep the surface cleanness and the STM stability enough long time (up to few days) to perform experiments on a single atom for days at a time. The same technique was used to manipulate CO molecules and Pt atoms on the Pt(111) surface [26, 27]. The most impressive Eigler's result is connected with an artificial structure called "a quantum corral" [28]. A circular corral of a radius $\approx 7$ nm was assembled by individually positioning Fe adatoms on Cu(111) surface. The Fe adatoms act as high wall potential barriers for surface states of electrons on Cu(111), and new quantum states are created. The circular standing waves of the surface state electrons inside the corral (Fig. 7) arise from

Fig. 5. STM images of Cs on p-type GaAs(110) surfaces illustrating the field assisted diffusion before pulsing the voltage (A through C), and after pulsing the sample voltage to $+1$ V (D through F). The inset in (A) shows an atomic resolution $7 \times 7$ nm$^2$ image of the Cs zigzag structure on GaAs (in the centre). Reprinted with permission from [25] (L.J. Whitman, J.A. Stroscio, R.A. Dragoget, R.I. Celotta, Science 251, 1206 (1991)). Copyright 1991 American Association for the Advancement of Science.
their confinement, which forces the electrons into a new set of quantum states. Tunneling spectroscopy performed inside of the corral \((dI/dV\) spectra vs. bias voltage) provided an evidence for size quantization.
The perpendicular processes in general rely on the atom or molecule transfer from the surface to the tip or vice versa at a desired position. An important energy for such processes is the height of the energy barrier that the adsorbate must traverse to be adsorbed or deposited at a given spot. This class of processes is divided into (i) transfer on- or near-contact and (ii) field evaporation.

(i) The transfer-on-contact may be realized when the adsorption wells on the tip and surface sides of the junction coalesce, that means that the barrier separating two wells disappears. An adsorbed atom or molecule is bound to the tip and the surface at the same time. If the binding energy to the tip is greater than to the sample, the adsorbate follows the tip when the tip is withdrawn out of the surface. If a controlled reversible motion of an atom between the tip and surface could be achieved, e.g., by the application of electrical signal, an atomic-scale bistable electronic switch could be developed. Eigler et al. [29] have shown such “an atomic switch” realized with Xe atom jumping between the STM tip and Ni surface. When the tip and the sample are not “in contact” (as above) but are close enough each other to reduce the intermediate barrier, “transfer-near-contact” of an adsorbate atom may take place due to the thermal activation. The rate of this process is proportional to $\nu \exp\left(-Q/kT\right)$, where $\nu$ is the frequency factor, $Q$ is the reduced barrier between the tip and the sample, $k$ is Boltzmann’s constant, and $T$ is the absolute temperature. A transfer rate of $1 \text{ s}^{-1}$ is obtained with a barrier reduced to about 0.75 eV, with $\nu \approx 10^{13} \text{ s}^{-1}$ and $T = 300 \text{ K}$.

(ii) Field evaporation, contrary to transfer-near-contact, requires an intermediate ionic state. In general, field evaporation is described as a thermally activated evaporation of ions over a Schottky barrier formed by the lowering of the potential energy outside the conductor by the application of an electric field. Mamin et al. [9] demonstrated the ability to create ordered arrays of Au mounds on a Au surface.

Fig. 8. Schematic potential energy curves illustrating a chemically-assisted field evaporation process. The solid line represents the neutral ground state where an atom is bonded either to the substrate (left well) or to the tip (right well). The dashed line corresponds to an ionic state of the potential energy of an adsorbate as a function of its lateral position, (a) the case for a barrier of 1 nm width, (b) the case for a barrier width reduced to ca. 0.3 nm, (c) the barrier height for an ionic state is reduced further by applying a bias voltage between the STM tip and the sample.
by the application of 600 ns pulses +3.6 V applied to an Au surface. Cleary [30]
reported the possibility to remove an individual S atoms from MoS$_2$ surface by
applying a voltage pulse at room temperature. Avouris and Lyo [31] demonstrated
that Si atoms could be reversibly transferred between a Si surface and W tip at
room temperature in UHV. They explained the process in terms of “a chemically
assisted field evaporation”. Figure 8a shows qualitatively potential energy (PE)
curves of an atom bound to the surface of the sample or to the tip for the both
neutral and ionic states. The potential barrier may be reduced by bringing the tip
quite close to the sample (Fig. 8b) and some degree of chemical bond between tip
and sample is established. Applying the bias voltage influences the barrier shape,
especially for the ionic state. Finally, the close proximity of the tip to the surface
leads to a significant reduction of the field strength necessary to initiate material
transfer (Fig. 8c) as compared in the field ion microscope.

4. Clusters and other mesoscopic systems on surfaces

Clusters, which consist of a few to several hundred atoms, display new prop-
erties, different from the bulk crystal, because of their atomic structure, bond
length and bond character [8]. The considerable interest lies in the electronic struc-

Fig. 9. The periodic structure of gold clusters (10.0 nm apart each other) deposited on
Si(111); the scanned area is 50 x 50 nm$^2$. 
ture of such formations [26, 32–34] as well as in the possibilities of manipulation and positioning at the atomic scale [24, 26, 27] because of expected applications in future nano-electronics. Clusters can be produced by gas expansion, ion bombardment, laser ablation of the material target [8] and deposited from the STM tip [9, 12].

Creation of regular arrays of Au clusters may serve as the first example. Figure 9 presents a linear arrangement of Au clusters of a well-controlled geometry (3.3 nm in diameter) with a periodic distance of (10.0 ± 0.1) nm. This structure was created by applying the sequence of voltage pulses between a gold STM tip and Si(111) surface in UHV and at room temperature. The details are reported elsewhere [12]. It was also shown that these structures were stable enough to ob-

![Image of STM images of selenium clusters arrays on HOPG substrate](image)

Fig. 10. STM images of selenium clusters arrays on HOPG substrate: (A) the rectangular arrangement of Se clusters (15 × 15 nm²), (B) the geometric model of the configurations for 6-members Se clusters on HOPG surface, (C) Se structures after applying a bias voltage of −0.7 V. The scanned area is 15 × 15 nm².
serve them even after few days in an unchanged configuration. This feature favours such cluster deposits for any future applications, because of their time stability and the avoidance of low temperature techniques. It is also noteworthy to mention that the $I$–$V$ characteristics measured above these clusters are non-linear (contrary to bulk gold samples), most probably due to their reduced dimensionality.

Regular, two-dimensional structures of Se clusters evaporated on HOPG are shown on Fig. 10A. The pattern indicates a regular rectangle structure with the lattice constants $\approx 0.72$ nm and $\approx 0.85$ nm, which coincides with three times of binary and bisectric distances of the hexagon in graphite. The molecules average diameter is $(0.53 \pm 0.05)$ nm and is comparable to the value found for Se$_6$ rings in a monoclinic crystal. Figure 10B shows the geometrical model of selenium 6-membered molecules arrays on HOPG, as deduced from our STM data. These regular Se cluster structures could be locally modified after applying the bias polarization below the threshold voltage, 0.7 V. The oval shaped islands with a diameter about 5 nm and 2 nm in height are created (Fig. 10C). One of possible explanations is that these islands are aggregates of selenium molecules after field-assisted diffusion or/and selenium atoms chains after breakdown of Se ring structure [35].

STM images of HOPG often reveal unusual structural features such as anomalous corrugation and asymmetry corrugation of neighbour atom sites [36]. Superperiodic lattice images are also observed in STM images. These patterns have hexagonal symmetry and larger periodicity of a few nm to several tens nm. The origin of this effect is attributed to a modulation of electronic structure caused by an interaction of the misoriented top layer of HOPG with under layer, like Moire patterns. This modulated electronic structure may serve also as a factor ordering the clusters on HOPG surface. The superperiodic structure of HOPG and the array of Sb clusters deposited by laser ablation are presented in Fig. 11A and B, respectively. Antimony clusters, previously randomly distributed on HOPG surface, were found to be adsorbed along the edge of superperiodic pattern with the same periodicity as one can observe for the Moire pattern, after the sample annealing at 600°C [32].

The final example of cluster modifications and manipulations is connected with fullerenes. Fullerenes as $C_{60}$ and $C_{70}$ are intensively studied from 1990 when Kratschmer and co-workers [37] have obtained a benzene solution of fullerenes. Lately, the possibility to obtain polymerized fullerenes as well as smaller structures due to laser irradiation has been pointed out [38]. Kasuya et al. [13] have studied the surface structures obtained by laser ablation (LA) of thin $C_{60}$ film onto HOPG and Si(111). Using STM we observed a variety of carbon clusters obtained on HOPG surface as it can be seen on Fig. 12A. It is plausible that clusters with a diameter up to 5 nm are the products of coalescence of $C_{60}$ particles and their fragments, produced during laser irradiation process, including higher fullerenes, e.g., $C_{120}$, $C_{180}$, etc. The obtained material exhibits semiconducting properties with the gap between 1.5–2 eV and STM imaging of an ultra thin layer of these clusters was possible above ca. 1 V threshold. With a decrease in the applied bias voltage down to 0.3 V we were able to induce some nanometer-scale structures by a material removal from a desired spot. Some examples of such structures are shown.
Fig. 11. STM images of $100 \times 100 \text{ nm}^2$ are of (A) the superperiodic structure observed on HOPG surface and of (B) Sb clusters (small white dots) array adsorbed along HOPG superperiodic structure.

Fig. 12. STM images of carbon clusters obtained on HOPG surface after laser ablation of $\text{C}_6\text{O}$ target (A) $25 \times 25 \text{ nm}^2$, (B) nanometer-scale modifications of carbon clusters layer created by STM tip according to the procedure presented in the text.

in Fig. 12B. Likely on HOPG, a variety of carbon clusters were observed on Si(111) surface. Clusters of 1 nm in diameter, typical of individual $\text{C}_6\text{O}$, as well as larger particles, which may be interpreted as higher fullerenes, are observed in Fig. 13A and B. $\text{C}_6\text{O}$ and other fullerenes may create a regular structures on many metal and semiconductor surfaces. Usually the first monomolecular layer is not ordered but the second or third one becomes ordered usually with the close packing fcc(111) configuration [39]. Another interesting example of $\text{C}_6\text{O}$ modifications was shown by Wawro et al. [40]. First, a regular film (three or four monolayers) of $\text{C}_6\text{O}$ was obtained on Si(111) surface. The structure was irradiated by KrF excimer laser. The STM image (Fig. 14) shows locally linear structures, which may be interpreted
as a chain of polymerized fullerenes. These structures were stable in time, however they could be re-modified to undisturbed fcc structure by applying a given bias polarization to the STM tip.

5. Concluding remarks

The nanoclusters and single atoms are the potential "bricks" that will be used to create the various devices of a very high degree of miniaturization. Most probably, it will be necessary to place small nanometer-scale structures in a desired position with subnanometer accuracy during the production processes of near-future electronic devices, especially memory elements. SPM techniques seem to be most suitable for creating or synthesizing "custom" made structures. It
should be possible to create artificial systems or phases of matter which do not exist normally in nature. The same instruments, after creating these structures, can be used for their imaging and for investigations of electronic properties of these new structures. The wide perspectives are opening in front of molecular synthesis and investigations of forces acting between atomic or molecular reactants. The atomic force microscope may be used to image and manipulate conducting species on insulating surfaces, etc. The strong influence of scanning probe methods on modern solid state science and technology has become evident. Instruments based on scanning probe microscopy and related techniques will be inherently present in the coming age of nanotechnology.

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