Abstract

An overview is given on electronic properties of flat and curved MoS$_2$ crystals. In the first part, scanning tunneling microscopy and spectroscopy methods are presented. Then structure and electronic properties of molybdenum disulfide crystal, nanotubes and fullerenes are described. Finally, we present our experimental results.
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1 Scanning tunneling microscopy (STM)

STM is a technique for viewing surfaces at atomic level. First scanning tunneling microscope was made in 1981 by Gerd Binning and Heinrich Rohrer. Typical resolution for STM is 0.1nm in lateral direction and 0.01nm in depth. STM probes the local density of states (LDOS) of a material by measuring tunneling current. The density of states of a system describes the number $N$ of states at each energy level $\epsilon$ that are available to be occupied.

$$g(\epsilon) = \frac{dN}{d\epsilon}$$  \hspace{1cm} (1)

Tunneling current depends on distance between sample and tip exponentially. The net current due to an applied voltage between sample and tip depends on two factors: 1) the number of electrons near Fermi energy, which have enough energy to tunnel through the barrier, and 2) the number of corresponding free states to tunnel into on the other side of barrier at the tip. The higher density of available states increases the tunneling current. When $V$ is positive, electrons in the tip tunnel into empty states in the sample; for a negative bias, electrons tunnel out of occupied states in the sample into the tip. Scanning tunneling microscope (STM) contains scanning tip, piezoelectric controlled height and x-y scanner, coarse sample-to-tip control, vibration isolation control and computer.

STM operates in two modes; constant current and constant height mode. In constant current mode, feedback electronics adjust the height by a voltage to the piezoelectric height control mechanism keeping the tunneling current constant. The image comes from voltage variations.

In constant height mode, the voltage and height are both held constant while the current is measured; this leads to an image made of current changes over the surface.

![Schematic view of a scanning tunneling microscope](image.png)

Figure 1: Schematic view of a scanning tunneling microscope [5].
2 Scanning tunneling spectroscopy (STS)

STS is a powerful experimental technique in scanning tunneling microscopy (STM) that uses a scanning tunneling microscope to probe the local density of states (LDOS) and band gap of surfaces at the atomic scale. Generally, STS involves observation of changes in constant-current topographies with tip-sample bias, local measurement of the tunneling current versus tip-sample bias \((I-V)\) curve, and measurement of the tunneling conductance \((dI/dV)\). Since tunneling current in a STM is a sum of electrons originating typically from a region with diameter \(\sim 5\AA\), STS is unique in comparison with other spectroscopy techniques, which average over a larger surface region.

Understanding the scanning tunneling spectroscopy is very important for \(I-V\) data interpretation. Using the modified Bardeen transfer Hamilton method, which treats tunneling as a perturbation, the tunneling current \(I\) is found to be

\[
I = \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} [f(E_F - eV + \epsilon) - f(E_F + \epsilon)] \rho_S(E_F - eV + \epsilon) \rho_T(E_F + \epsilon) |M_{\mu\nu}|^2 d\epsilon, \tag{2}
\]

where \(f(E)\) is a Fermi distribution function, \(\rho_S\) is density of states in the sample and \(\rho_T\) is density of states (DOS) in the tip. \(M_{\mu\nu}\) is the tunneling matrix element between the modified wave functions of the tip and sample surface:

\[
M_{\mu\nu} = -\frac{\hbar}{2\pi} \int (\chi^*_\nu \nabla \psi_\mu - \psi_\mu \nabla \chi^*_\nu) \cdot dS, \tag{3}
\]

\(M_{\mu\nu}^2\) describes the possibility for tunneling between modified wavefunctions \(\psi\) and \(\chi\). Here \(\psi\) and \(\chi\) are the sample wave function modified by the tip potential and the tip wave function modified by sample potential, respectively. For low temperature and constant tunneling matrix element, the tunneling current depends on:

\[
I \propto \int eV \rho_S(E_F - eV + \epsilon) \rho_T(E_F + \epsilon) d\epsilon. \tag{4}
\]

The tunneling current is a convolution of the DOS of the tip and the sample. So, if we want to know the DOS of sample, the tip DOS must be known. If we assume that the DOS of tip is constant, we obtain that the tunneling conductance is directly proportional to the DOS of sample.

\[
\frac{dI}{dV} \propto \rho_S(E_F - eV + \epsilon), \tag{5}
\]

2.1 Experimental methods

Several techniques exist to obtain the sample density of state, respectively \(dI/dV\).

- Acquiring standard STM topography at many different tip-sample biases and comparing the resulting topographic information is perhaps the most straightforward spectroscopic method. This method is quick way to determine whether there are any interesting bias-dependent features on the surface.
• Modulation technique: A small, high frequency sinusoidal modulation voltage is superimposed on the DC tip-sample bias. The AC component of the tunneling current is recorded using a lock-in amplifier, and the component in-phase with the tip-sample bias modulation gives $dI/dV$ directly.

• To obtain $dI/dV$ indirectly, we can measure $I(V)$ curve and then calculate $dI/dV$. There are two ways to record $I - V$ curves in the manner described above. In constant-spacing scanning tunneling spectroscopy (CS-STS), the tip stops scanning at the desired location to obtain an $I(V)$ curve. The tip-sample spacing is adjusted by desired initial current. A sample-and-hold amplifier freezes the z-piezo feedback signal, which holds constant tip-sample distance. After that the tip-sample bias voltage is swept through the specified values, and the tunneling current is recorded. The other way is variable-spacing scanning tunneling spectroscopy (VS-STS), the same steps occur as in CS-STS through turning off the feedback. As the tip-sample bias is swept through the specified values, the tip-sample spacing is decreased continuously as the magnitude of the bias is reduced. VS-STS is useful for conductivity measurements on systems with large band gaps.

Current-imaging-tunneling spectroscopy (CITS) is an STS technique where an $I(V)$ curve is recorded at each pixel in the STM topography. Either variable-spacing or constant-spacing spectroscopy may be used to record $I - V$ curve. The conductance, $dI/dV$, can be obtained by numerical differentiation of $I$ with respect to $V$.

3 The crystal structure of molybdenum disulfide

Molybdenum disulfide MoS\textsubscript{2} is a typical compound of the family of layered chalcogenides. The Mo atoms have a six-fold coordination environment and are hexagonally packed between two trigonally coordinated atomic layers of sulphur atoms. Depending on the arrangement of the S-atoms two kinds of the hexagonal S-Mo-S triple layers are possible, which are composed by either prismatic D\textsubscript{3h}\textsuperscript{h}- or octahedral O\textsubscript{h}\textsuperscript{h}-MoS\textsubscript{6} units. The S-Mo-S layers interact by weak van der-Waals interaction. Such triple layers may be stacked in different ways. Natural MoS\textsubscript{2} occurs as a mixture of two stable polymorphs based on D\textsubscript{3h}-MoS\textsubscript{6} units, the hexagonal 2H-MoS\textsubscript{2} and the rhombohedral modification 3R-MoS\textsubscript{2}. The unit cell of 2H-MoS\textsubscript{2} and 3R-MoS\textsubscript{2} contain two and three alternating S-Mo-S layers, respectively. The 2H-polytype is more stable than 3R-polytype. The 3R-type transform into the 2H-type upon heating.

A meta-stable material based on octahedral O\textsubscript{h}-MoS\textsubscript{6} unit is 1T-MoS\textsubscript{2} allotrope. 1T-MoS\textsubscript{2} does not exist in nature, but can be obtained by an intercalation of 2H-MoS\textsubscript{2} crystals with alkali metal atoms and subsequent salvation of the intercalates with the formation of 1T-MoS\textsubscript{2} layers.
Figure 2: Schematic presentation of a 2H and 1T type bulk structure [5].

Figure 3: 2H- and 3R-MoS$_2$ polytypes (1) and (2) based on the layers composed by prismatic MoS$_6$ units (4). 1T-MoS$_2$ modification (3) based on the layers composed by octahedral MoS$_6$ units (5). The unit cells are detached [2].
3 THE CRYSTAL STRUCTURE OF MOLYBDENUM DISULFIDE

3.1 The electronic structure of MoS2 crystal

In the electronic structure of 2H-MoS2 polytype both experimental and quantum-mechanical methods (augmented-spherical-wave method) clearly distinguish three bands. The lowest band of the S3s-states is separated from the valence band by a wide gap. The states near the Fermi level are mainly Mo4d-states. More close to the bottom of the valence band mixed Mo4d- and S3p-states occur. The bottom of the conduction band is composed of Mo4d-states. Therefore, 2H-MoS2 is a semiconductor with indirect band gap. Experimental value of the gap is approximately 1 eV. The density of states of the 3R-MoS2 polytype is similar to 2H-MoS2.

In the octahedral modification the bands are grouped into a set of Mo4dr-states overlapping with filled sets of S3sp-bands and a set of low lying S3s-band; the degenerate Mo4dxy,yz,xz-orbitals from a single set of bands populated by two electrons, which leads to the metallic ground state of the system.

Figure 4: Electronic structure of MoS2: Band structure of 2H-MoS2 (1), qualitative band diagrams of MoS2 slabs based on D3h-MoS6 and Oh-MoS6 units (2) [2].

Detailed experimental studies of 1T-MoS2 electron diffraction, and scanning tunneling microscopy have provided evidence that it is not released as monolayers with an ideal elementary cell of a x a lattice constants, but rather superstructures such as 2a x 2a, √3a x √3a and 2a x a are obtained. Calculation indicated that a further elongation in the plane of a 1T-MoS2 monolayer opens the gap in the valence band and the compound loses its metallic properties. The required energy for this change is low which is in agreement with the meta-stable character of the 1T-phase.

The 2H-MoS2 is similar to silicon with respect to its electronic properties. Indirect and direct band gaps are 1.29eV and 1.95eV for 2H-MoS2, respectively. A gap for silicon is 1.2V. The S-Mo-S layers are very resistant to the ambient (to oxidation and humidity effects). This inertness may be very important in nano-sized particles, when the reactivity...
The specific surface of the compounds usually increases because of the high specific surface. It constitutes a considerable advantage of MoS$_2$ compared with semiconductors of the groups IV (e.g. Si), III-V (e.g. GaAs), II-VI (e.g. CdS) and can make MoS$_2$ the compound of choice in nanoscale applications, which demand a long life time.

4 MoS$_2$ nanotubes

Tubular structures can be constructed by conformal mapping of a 2D triple layer of MoS$_2$ onto the surface of a cylinder, thus rolling up the sheets along specific direction in the 2D lattice. This may be described in terms of the primitive 2D lattice vectors $\vec{a}$ and $\vec{b}$, and two integer indices $(n, m)$: $\vec{B} = n\vec{a} + m\vec{b}$. In this way three classes of nanotubes can be distinguished: $n = m$ armchair nanotubes, $n \neq 0, m = 0$ zigzag nanotubes, and $n \neq m$ chiral nanotubes. Nanotubes have one S-Mo-S layer (single-walled nanotube) or more than one triple layer (multi-walled nanotube).

The nanotubes with diameter ($D$) ranging between 8Å and 26Å, which correspond to indices $(n, 0) - (n, n)$ from $(10, 0) - (6, 6)$ to $(22, 0) - (14, 14)$, respectively. For nanotubes with diameter 26Å, the optimized bond lengths are slightly larger than those of the planar sheet. The Mo-S bond length within the inner shell is increased by approximately 0.01Å and the Mo-S bond length on the outer shell increases by 0.04Å. The Mo-Mo distance is greater than that of the flat sheet by nearly 0.25Å. The calculated strain energy follow roughly a $1/D^2$ behavior.

4.1 The electronic structure of MoS$_2$ nanotubes

The main features of the calculated density of states (DOS) curves are quite similar for all tubes and also similar to that of the planer triple layer. The DOS is characterized by a well separated peak corresponding to a sulphur s band of about 2eV width and 14 eV below the valence band edge. This is followed, at higher energy, by the valence bands with a width of about 7 eV, formed by hybridized Mo d and sulphur p states. The corresponding antibonding states characterize the conduction band. The Mo d states especially dominate the upper valence band edge as well as the lower conduction band edge. These features are in agreement with results from band structure calculations for bulk MoS$_2$. The gap size increases with increasing tub diameter, but still being smaller than the gap for a single flat triple layer and the bulk material.

All MoS$_2$ nanotubes have a nonzero direct gap and indirect gaps down to the smallest tubes, which increase smoothly with increasing diameter. The size of indirect gap for the $(n,n)$ tubes is close to that of the direct gaps of the $(n,0)$ tubes with similar diameter.

The zigzag nanotubes possess a small direct gap. This suggests that zigzag nanotubes can be used for optoelectronics (luminescing devices).
Figure 5: Armchair (8,8) MoS$_2$ nanotube (left) and zigzag (14,0) MoS$_2$ nanotube (right). Dark atoms are Mo, and light atoms are S [1].
Figure 6: Calculated stain energies of MoS$_2$ nanotubes as a function of tube diameter in Å (left). Calculated gap energies of MoS$_2$ nanotubes as a function of tube diameter in Å (right) [1].

Figure 7: Calculated band structure for a MoS$_2$ zigzag (22,0) nanotube (left). Calculated band structure for a MoS$_2$ armchair (14,14) nanotube [1].
5 MoS$_2$ Fullerenes

MoS$_2$ fullerenes are another nanosized allotrope of molybdenum disulfide. They are hollow and have an irregularly faceted shape (even quasi-spherical to the first approximation) with radii of up to some tens of nanometers. Similar to the MoS$_2$ nanotubes MoS$_2$-based fullerene-like particles obtained experimentally are always composed of several nested shells, therefore they have also been addresses as onion-like particles or Russian doll fullerenes. The mono-layers, which form the shells of these particles, are partially curved layers of the 2H-MoS$_2$ allotrope. The density of states for MoS$_2$ fullerenes is quite similar in profile to those of semi-conducting nanotubes and bulk MoS$_2$. The general features of the electronic spectra are the same in all cases. The valence band is composed of mixed Mo$4d$-S$3p$-states.

![Image of MoS$_2$ fullerene](image.png)

Figure 8: A high resolution transmission electron microscopy image of typical fullerene-like MoS$_2$ particle[12].

6 Experimental results

We studied two samples by scanning tunneling microscope. First sample was 2H-MoS$_2$ crystal, and the second were MoS$_2$ fullerenes and nanotubes on HOPG (high oriented pyrolytic graphite). We used a tungsten tip, which was prepared by electrochemical etching.

6.1 Topography of MoS$_2$ fullerene

When we have been measuring the spectroscopic curves for MoS$_2$ we obtained the topography image of them, too. We succeeded to obtain the first atomic resolution image on a MoS$_2$ fullerene.
Figure 9: 3D view of MoS2 fullerene (A), topography of surface of fullerene (B), and profile in three direction on the surface (C).
6.2 $I-V$ spectroscopy and conductivity of MoS2 crystal and MoS2 fullerenes

All of $I-V$ curves were observed by constant-spacing scanning tunneling spectroscopy (CS-STS) method. The distance between sample and tip was adjusted by bias voltage between tip and sample. Distance is dependent on bias voltage and conductivity of sample. Our measurement conditions were $U_{\text{gap}} = 1.0V$, and $I_{\text{setpoint}} = 1.0nA$.

Every spectroscopic curve (figure 10,11) is an average of many single measurements. We obtained 50 I-V curves for MoS$_2$ and 400 for HOPG, respectively. A single $I-V$ curve is typically very noisy. An average over a lot of measurements decreases noise. This averaged result we differentiated and obtained a conductivity curve, which is proportional to density of states.

The features of $I-V$ curve of MoS$_2$ crystal and MoS$_2$ fullerene are almost identical. Conductivity curves have semi conducting behavior, with band gap approximately 1.5eV.

![I-V spectroscopy and Conductance of MoS2](image)

Figure 10: $I-V$ Spectroscopy of MoS$_2$ crystal and fullerene ($U_{\text{gap}} = 1.0V$, $I_{\text{set}} = 1.0nA$) (left). Conductivity curve ($dI/dV$) (right).

6.3 $I-V$ spectroscopy and conductivity of HOPG

For comparison, we measured spectroscopic curves for graphite. We observed difference between $I-V$ curves for MoS$_2$ and graphite, as we expected. Conductibility curve for graphite have not band gap, which means that graphite is conductor, what is in accordance with literature data [13].
7 Applications of MoS₂

Molybdenum disulfide is used for electrodes in high-efficiency photo-electrochemical cells. It is useful for application in solar cells because it has large coefficient of absorption in visible spectrum of light. MoS₂ is known to be also extremely good solid lubricant. The weak inter-atomic interaction (van der Waals forces) between the MoS₂ molecular layers in the form of plate-like crystals allow easy, low-strength shearing in vacuum, but this property is worse in the presence of humidity or oxygen. MoS₂ can act as catalyst for desulfurization of oil. It has highly anisotropic physical properties. Hence it can be intercalated with foreign atoms. The intercalation of lithium has lead to its use in lithium batteries, while physisorption of hydrogen promise applications for energy storage.

Figure 11: $I−V$ Spectroscopy of HOPG ($U_{gap} = 1.0V$, $I_{set} = 1.0nA$) (left). Conductivity curve ($dI/dV$) (right).
References


