Controlled Deposition Of Magnetic Molecules And Nanoparticles On Atomically Flat Gold Surfaces

2008

Md. Firoze Haque

University of Central Florida

Find similar works at: https://stars.library.ucf.edu/etd

University of Central Florida Libraries http://library.ucf.edu

Part of the Physics Commons

STARS Citation

https://stars.library.ucf.edu/etd/3733

This Masters Thesis (Open Access) is brought to you for free and open access by STARS. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of STARS. For more information, please contact lee.dotson@ucf.edu.
CONTROLLED DEPOSITION OF MAGNETIC MOLECULES AND
NANOPARTICLES ON ATOMICALLY FLAT GOLD SURFACES

by

MD. FIROZE H. HAQUE
M.S. University of Cincinnati, 2003
B.Sc. University of Dhaka, 1997

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science
in the Department of Physics
in College of Science
at the University of Central Florida
Orlando, Florida

Major Professor: Enrique del Barco

Summer Term
2008
ABSTRACT

In this thesis I am presenting a detailed study to optimize the deposition of magnetic molecules and gold nanoparticles in atomically flat surfaces by self-assembling them from solution. Epitaxially grown and atomically flat gold surface on mica is used as substrate for this study. These surfaces have roughness of the order one tenth of a nanometer and are perfect to image molecules and nanoparticles in the 1-10 nanometers range. The purpose of these studies is to find the suitable parameters and conditions necessary to deposit a monolayer of nano-substance on chips containing gold nanowires which will eventually be used to form single electron transistors by electromigration breaking of the nanowire. Maximization of the covered surface area is crucial to optimize the yield of finding a molecule/nanoparticle near the gap formed in the nanowire after electromigration breaking. Coverage of the surface by molecules/nanoparticles mainly depends on the deposition time and concentration of the solution used for the self-assembly. Deposition of the samples under study was done for different solution concentrations and deposition times until a self-assembly monolayer covering most of the surface area is obtained. Imaging of the surfaces after deposition was done by tapping-mode AFM. Analysis of the AFM images was performed and deposition parameters (i.e. coverage or molecule/particle size distribution) were obtained. The subjects of this investigation were a molecular polyoxometalate, a single-molecule magnet and functionalized gold nanoparticles. The obtained results agree with the structure of each of the studied systems. Using the optimized deposition parameters found in this
investigation, single-electron transport measurements have been carried out. Preliminary results indicate the right choice of the deposition parameters.
DEDICATION

To all my family members, specially my father, mother, wife Fahmina Akhtar and my kid brother Mahrabul Hoque. Without their help and support this work would have been impossible. To my friends, for all their support.
ACKNOWLEDGMENTS

Special thanks to Physics Chair Talat Rahman for all her help and support. Also thanks to George Christou for the Mn$_{12}$ samples and Florencio Eloy Hernández for magnetic gold nanoparticle samples. Very special thanks to Masahiro Ishigami for so many useful discussions and suggestion to use epitaxially grown and atomically flat gold surface. Thanks to UCF’s Engineering Department for the help in their clean room and Brian Fisher for the help in the metal deposition. Thanks to CREOL and Ivan for assistance in fabrication of samples. Thanks to the UCF physics department for the access to the AFM and David Bradford for all the help in the machine shop.

Special thanks to Austin Coye for helping me with gold nanoparticle project and my lab mates John Henderson, Hajrah Quddusi and Simranjeet Singh.

Very special thanks to my Advisor Enrique del Barco for his support and dedication.
TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... ix

CHAPTER 1 INTRODUCTION ........................................................................................ 1
  1.1. Molecular Magnets .............................................................................................. 1
  1.2. Single-Molecule Magnets .................................................................................... 2
  1.3. Magnetic Gold Nanoparticles .............................................................................. 4
  1.4. Single Electron Transistors .................................................................................. 5
  1.5. Fabrication of Single Electron Transistor Devices .............................................. 8
  1.6. Atomic Force Microscope ................................................................................... 10
    1.6.1. Tapping Mode ............................................................................................... 12
    1.6.2. Gold Mica Substrates ................................................................................... 13

CHAPTER 2 POLYOXOMETALATE MOLECULAR MAGNET ................................ 16
  2.1. Chemical Structure .............................................................................................. 16
  2.2. Sample Preparation ............................................................................................. 17
  2.3. Data ..................................................................................................................... 18
    2.3.1. Deposited for 5 Minutes ............................................................................... 18
    2.3.2. Deposited for 11 Minutes ............................................................................. 19
    2.3.3. Deposited for 38 minutes ............................................................................. 20
    2.3.4. Deposited for 60 minutes ............................................................................. 21
  2.4. Discussion ............................................................................................................ 21
  2.5. Preliminary SET Studies ..................................................................................... 22

CHAPTER 3 Mn$_{12}$-ACETATE SINGLE MOLECULE MAGNET: ............................... 26
  3.1. Chemical Structure .............................................................................................. 26
  3.2. Sample Preparation ............................................................................................. 27
  3.3. Data ..................................................................................................................... 28
    3.3.1. Deposited for 6 minutes ............................................................................... 28
LIST OF FIGURES

Figure 1: Ball-and-stick model of the polyoxometalate: O (grey), Mo (blue), V (red), and P (yellow). ................................................................. 1

Figure 2: (A) energy representation of the anisotropy barrier of Mn_{12}-acetate, showing the energy levels corresponding to 2S+1 opposite spin projections along the easy magnetic axis of the molecule. (B) Graphic representation of single molecule magnet Mn_{12}. (C) Magnetization curve of Mn_{12}-acetate at T = 0.6 K. The jumps are due to resonant quantum tunneling at the resonance fields. The background shows the potential energy wells tilted by the action of a longitudinal field. ............................................. 3

Figure 3: (A) Schematic representation of a three terminal SET. (B) Energy representation of the electrostatic levels of the molecule with respect to the Fermi energies of the source and drain electrodes. N represents the molecule on its neutral charge state, being N+1 and N-1 its first reduction and oxidation states, respectively. Ec is the charging energy of the molecule. (C) The effect of a bias voltage on the energy configuration of the molecular SET. Note that the first exited state (N+1) of the molecule is now available for conduction, since it lies within the Fermi energies of the electrodes. 6

Figure 4: A) Calculated current for an ideal single-state molecular SET (upper A-C scheme) as a function of the bias voltage, $V$, for different gate voltages, $V_g$. B) $I$ and C) $dI/dV$ contour-plots of a single-level molecular SET calculated assuming asymmetric barriers and tunnel rates. The dashed color lines in B correspond to the $I$-$V$ curves shown in A. D) $dI/dV$ contour plot of an ideal double-level molecule (lower D scheme). ............ 8

Figure 5: A) Design perspective and B) photograph of our SET device. The chip on B is 1×1 cm$^2$ and contains 35 SETs grouped in five sets of six transistors each, as shown in A. The substrate is pure silicon with a one micrometer silicon oxide layer on top. C) AFM image of a zoomed area in the chip where the wire nanoconstriction and the Al gate are shown. D) SEM image of the gold nanowire. ................................................................. 9

Figure 6: Working principle of AFM in contact mode. ................................................................. 10

Figure 7: Working principle of tapping mode AFM where the cantilever and tip keep on vibrating at a certain frequency and map the surface from the variation of amplitude. ... 12

Figure 8: AFM image of E-beam evaporated gold surface on mica................................. 14

Figure 9: AFM image of (A) epitaxially grown gold on green mica, (B) Scope trace of the image showing height profile................................................................. 15

Figure 10: Ball-and-stick model of the polyoxometalate: O (grey), Mo (blue), V (red), and P (yellow) .................................................................................................................. 16
Figure 11: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 5 minutes. (b) Scope trace of the image showing height of the molecules. 18

Figure 12: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 11 minutes. (b) Scope trace of the image showing height of the molecules. 19

Figure 13: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 38 minutes. (b) Scope trace of the image showing height of the molecules. 20

Figure 14: AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 60 minutes. 21

Figure 15: (a) Breaking voltage and (b) current of nanowires as a function of low temperature resistance. 23

Figure 16: Typical breaking curve for a 10 nm tall 100 nm wide gold nanowire for this data set. 23

Figure 17: (a) Coulomb Blockade, the current goes to zero near zero S-D bias. (b) STP where we see steps in the conduction near zero bias indicating we may be near a changing charge state of the molecule. (c) SMT where we see an asymmetric curve about zero bias. 24

Figure 18: Breakdown of post-electromigration statistics based on 155 wires being broken. 25

Figure 19: The ball and stick model of Mn_{12}-acetate. (a) The entire molecule, with methyl groups replaced for clarity by hydrogen atoms (golden). Here, H (golden), O (red) and Mn (blue). (b) A different perspective magnetic core Mn_{12}O_{12} with inner four Mn^{4+} ions. 26

Figure 20: (a) AFM Image of Mn_{12}-acetate magnetic molecules on gold-mica surface deposited for 6 minutes. (b) Scope trace of the image showing height of the molecules. 28

Figure 21: (a) AFM Image of Mn_{12}-acetate magnetic molecules on gold-mica surface deposited for 10 minutes. (b) Scope trace of the image showing height of the molecules. 29

Figure 22: (a) AFM Image of Mn_{12}-acetate magnetic molecules on gold-mica surface deposited for 20 minutes. (b) Scope trace of the image showing height of the molecules. 30

Figure 23: (a) AFM Image of Mn_{12}-acetate magnetic molecules on gold-mica surface deposited for 32 minutes. (b) Scope trace of the image showing height of the molecules. 31
Figure 24: (a) AFM Image of Mn₁₂-acetate magnetic molecules on gold-mica surface deposited for 47 minutes. (b) Scope trace of the image showing height of the molecules. ........................................................................................................................................... 32

Figure 25: I-V curves of single or multiple molecules for different gate voltages (device-I)........................................................................................................................................ 34

Figure 26: dI/dV as function of bias and gate voltage in a contour plot (Device-I). . . . 35

Figure 27: dI/dV as function of bias and gate voltage in a contour plot (Device-II).... 36

Figure 28: AFM image of molecules on gold-mica substrate deposited from three day old solution in different areas (a, b, c) showing ring formation................................. 39

Figure 29: Diameter distribution of the Mn₁₂-acetate rings deposited from three day old solution............................................................................................................................. 39

Figure 30: Height distribution of the Mn₁₂-acetate rings deposited from three day old solution............................................................................................................................. 40

Figure 31: AFM image of molecules on gold-mica substrate deposited from fresh solution in different areas (a, b, c) showing ring formation. .............................................................. 42

Figure 32: Height distribution of the Mn₁₂-acetate rings deposited from fresh solution. 42

Figure 33: 3D presentation of the AFM image of molecules on gold-mica substrate deposited from three day old solution (Figure. 28c)............................................................... 43

Figure 34: 3D presentation of the AFM image of molecules on gold-mica substrate deposited from fresh solution (Figure. 29c). ............................................................................. 44

Figure 35: The structure of functionalized gold nanoparticle is represented by a stacking model of red balls. The capping molecules are also shown using a ‘ball–stick’ model: hydrogen (white), carbon (grey), nitrogen (blue), oxygen (green) and sulfur (yellow). .. 45

Figure 36AFM images of nanoparticles deposited from (a) 1:25 and (b) 1:50 diluted solution.............................................................................................................................. 47

Figure 37: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 16 minutes. ..................................................................................... 48

Figure 38: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 37 minutes. .......................................................................................... 49

Figure 39AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 64 minutes. .......................................................................................... 49

Figure 40: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 400 minutes. ................................................................................... 50
Figure 41: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 1100 minutes ................................................................. 50

Figure 42: Height distribution of the magnetic gold nanoparticles deposited from 1:100 diluted solution................................................................. 51
1.1. Molecular Magnets

Molecules with magnetic ions ordered by exchange interaction, showing a ground spin state at low temperature are recognized as molecular magnets. Such a molecule is \([\text{PMo}_{12}\text{O}_{40}(\text{VO})_2]^{\text{q-}}\) \(^{[1]}\) (figure 1) a polyoxometalate\(^{[2]}\) which consists of a central mixed-valence core based on the \([\text{PMo}_{12}\text{O}_{40}]\) Keggin \(^{[3]}\) unit, able to act as an electron reservoir accommodating a variable number of delocalized electrons hopping over the Mo centers, capped by two vanadyl groups containing two localized spins. The spins on these two \((\text{VO})^{2+}\) units in general are weakly magnetically coupled via the delocalized electrons of

Figure 1: Ball-and-stick model of the polyoxometalate: O (grey), Mo (blue), V (red), and P (yellow).
the central core. For the description of the low-energy states of the polyoxometalate, two cases have to be distinguished: For an even number of electrons on the mixed-valence Keggin core, their spins pair antiferromagnetically to form a total spin 0 state. Then the system can be modelled by the two spins 1/2 on the vanadyl groups weakly coupled via an indirect exchange mechanism mediated by the core electrons. On the other hand, if the number of core electrons is odd, an unpaired spin 1/2 on the core remains and one obtains a set of three coupled spins 1/2 restricting ourselves to two charge states differing by one electron. So the state of the molecule can be changed by changing the number of electrons in the core. Using this molecule an experimental setup has already been proposed to do quantum computation [4].

1.2. Single-Molecule Magnets

Single Molecule Magnets (SMMs) are a class of molecules containing multiple transition-metal ions bridged by organic ligands. These ions are strongly coupled by exchange interaction, often in a ferrimagnetic manner, yielding large magnetic moments per molecule. The large spin, combined with a zero-field splitting, provides an anisotropy barrier to magnetization reversal (figure 2B). SMM crystals offer several advantages relative to other magnetic structures. Most importantly, they are monodisperse: All molecules in the crystal have identical spin amplitude and orientation, magnetic anisotropy, and atomic constituents and are weakly interacting with respect to each other. Monodispersity enables the study of behavior that is intrinsic to the magnetic nanostructure and which has been experimentally inaccessible in other classes of magnetic materials. Particularly important is the appearance of quantum tunneling
between opposite spin projection levels of the molecule, which leads to step-wise magnetic hysteresis loops and accelerated magnetic relaxation at fields that switch on the quantum tunneling mechanism [5, 6]. Another advantage involves the weak coupling between the molecule's spin levels and the environment. SMMs also provide opportunities to probe the realm that borders quantum and classical physics, as well as study decoherence phenomena in quantum systems [7, 8]. Technologically, these systems have several potential applications, including quantum computation and quantum information storage [9]. Moreover, by containing a single bit per molecule, SMMs represent the ultimate classical limit in magnetic information storage. Thus, they are promising candidates for future magnetic data storage media with an improvement in storage density by several orders of magnitude in comparison with current technologies. Understanding the relationship between the quantum properties of these materials and their structural characteristics will require the synthesis of new complexes with desirable properties.
properties, which will, in turn, allow in-depth studies on the fundamental aspects of nanoscale physics and quantum information processing.

Figure 2B shows the spatial disposition of the magnetic (Mn) ions in the prototype and most widely studied SMM, Mn$_{12}$-acetate. This molecule has a central core of four Mn$^{4+}$ ions ($S = 3/2$, green) surrounded by a ring of eight Mn$^{3+}$ ions ($S = 2$, yellow). The central ions are ferromagnetically coupled and the central core is antiferromagnetically coupled with the outer ring, giving rise to a net spin $S = 10$ at low temperatures ($T < 30$ K). Currently, more than a hundred different SMMs, with ground spin states ranging from $S = 0$ (antiferromagnetic) to $S > 30$, have been obtained and magnetically characterized.

1.3. Magnetic Gold Nanoparticles

Metallic nanoparticles are of high current interest for application in several areas of energy technologies. Their characteristic quantum properties associated to their limited size allow tuning of their response by selectively on frequency, particle size and fictionalization. Gold nanoparticle are known to respond to specific light frequencies (plasmonic resonance) depending particle size. Recently, it has been observed that when functionalized in a certain manner. The plasmonic resonance vanishes. This phenomenon has been associated to an induced ferromagnetization on the gold nanoparticle, which makes these systems of great interest as multifunctional materials for future technological applications. This phenomenon has been observed in ensembles of particles, where the magnetization has been measured. Our current interest is to measure an individual particle by means of Single Electron Transfer (SET) devices.
1.4. Single Electron Transistors

Electronic transport properties of individual molecules have received considerable attention over the last several years due to the introduction of single-electron transistor (SET) devices [10-22]. A scheme of a three-terminal SET is represented in figure 3A. The molecule is placed between three electrode leads (source, drain, and gate). The electrostatic coupling between the molecule and the leads is of a capacitive nature, since the ligands surrounding the molecule act as insulating barriers. The capacitances depend primarily on the molecule/lead distances, but also on the molecule's ligand composition. While placed far from the gate, ligands attach the molecule to source and drain electrodes and provide tunneling barriers for the electron to move in and out of the molecule. Therefore, an electric current can flow between the source and drain electrodes through a sequential tunneling process. Figures 3B and 3C represent the energy landscape of an ideal molecular SET. The black regions on the sides represent the electron Fermi seas in the source and drain electrodes, with $\mu_S$ and $\mu_D$ being the Fermi levels of the leads. The grey blocks represent the tunnel barriers between the molecule and the source/drain leads (note that these barriers can be quite asymmetric since the disposition of the molecule with respect to the electrodes may vary). The charge states of the molecule are represented by the horizontal lines in between the barriers. The highest of all occupied states (solid lines) represents molecule with $N$ electrons and an electrochemical
Figure 3: (A) Schematic representation of a three terminal SET. (B) Energy representation of the electrostatic levels of the molecule with respect to the Fermi energies of the source and drain electrodes. $N$ represents the molecule on its neutral charge state, being $N+1$ and $N-1$ its first reduction and oxidation states, respectively. $E_c$ is the charging energy of the molecule. (C) The effect of a bias voltage on the energy configuration of the molecular SET. Note that the first exited state ($N+1$) of the molecule is now available for conduction, since it lies within the Fermi energies of the electrodes.

potential $\mu_N$. The first (empty) excited state is separated by an energy $E_c + \Delta E$, where $\Delta E$ is the electrodes may vary). The charge states of the molecule are represented by the horizontal lines in between the barriers. The highest of all occupied states (solid lines) represents the molecule with $N$ electrons and an electrochemical potential $\mu_N$. The first (empty) excited state is separated by an energy $E_c + \Delta E$, where $\Delta E$ is the molecular electronic level spacing and $E_c$ is the energy necessary to add one electron into the molecule (charging energy or redox potential). Conduction through a molecular SET only occurs when a molecular electronic level lies between the Fermi energies of the leads. A bias voltage $V$ applied between the source and the drain moves the Fermi level of one of the leads by $|eV|$. For small bias voltages, $|eV| < E_c + \Delta E$, no current flows though the device because the excited molecular levels are not available to accept conduction electrons (figure 3B).
As the bias voltage is further increased, excited states open new conduction channels through the device. Abrupt and discrete changes in the current through the SET will be obtained every time a new molecular level becomes energetically accessible. The voltage values at which these current steps occur can be tuned by a potential applied to the gate electrode, $V_G$, which moves the molecular states with respect to the Fermi levels of the electrodes.

Coulomb blockade and the characteristic conduction behavior of an SET are illustrated in figure 4, where numerical calculations of the current flowing through an ideal SET are presented. Figure 4A shows the typical $I$-$V$ curves observed in a SET at different gate voltages. Discrete steps are observed whenever a new excited state is accessible for conduction. Contour plots of the current (figure 4.B) and the current derivative (figure 4C) as functions of the bias and gate voltages show the characteristic diamond structure representative of Coulomb blockade. Figure 4.C illustrates how two consecutive charge states of the molecule ($N$ and $N+1$) are separated by excitation lines. These lines intersect at the point where the gate voltage is equal to the charging energy of the molecule. The $dI/dV$ plot of an SET also reveals the level structure of the molecule and thus constitutes a powerful spectroscopy technique to study the energy landscape. Typically, the transition region between two charge states of the molecule contains multiple excitations that can be traced to the molecule’s energy levels. For example, figure 4D shows the differential
conductance of a molecule where the current flows through two levels of the first excited charge state. As in other spectroscopic techniques, the position, the shape, the magnitude, and the slope (among others) of the conduction excitations unveil characteristics that are both intrinsic (i.e., the electronic nature of the molecule) and extrinsic (i.e., the disposition of the molecule with respect to the electrodes) of the system under study.

1.5. Fabrication of Single Electron Transistor Devices

Measuring electrical conduction through an individual molecule is not a straightforward task. The main difficulty is the impossibility of obtaining electrodes separated by just a few nanometers (< 3 nm) using conventional lithographic techniques. There are several approaches that try to circumvent this problem. Scanning probe microscopy techniques, such as STM [23-26] or AFM [27] have been widely used to study the conduction through individual molecules deposited on a metallic surface. However, this approach requires sophisticated instrumentation, extensive expertise in low-temperature
techniques, and cannot make use of a gate electrode to study the different charge states of the molecule. Alternative approaches involve the on-chip fabrication of nm-size gap electrodes. There are several such methods: The mechanical break junction technique [28] (where a suspended nanowire is broken by stress applied to the substrate), the electrodeposition technique [20] (where a large gap is reduced by electrodeposition), the electromigration technique [22] (where a metal nanowire is broken by a current), and others (Refs. [11-21]). Deposition of the nano-size particle is an important step in the process. To get a single nanoparticle or molecule in the gap it is very important. So the study of assembling them is necessary. It’s also very important to increase the yield of the process which is very low (5-10%).

At University of Central Florida we use the electromigration induced breaking of nanowire to from the transistor. The chip with the nanowires is prepared with the help of lithography technique on oxidized doped silicon substrate. The insulating top silicon dioxide layer is ~ 250 nm thick. Gold contact pads, connecting wire and aluminum gate with smallest feature size of 6 µm are patterned using several step of photolithography.

Figure 5: A) Design perspective and B) photograph of our SET device. The chip on B is 1×1 cm² and contains 35 SETs grouped in five sets of six transistors each, as shown in A. The substrate is pure silicon with a one micrometer silicon oxide layer on top. C) AFM image of a zoomed area in the chip where the wire nanoconstriction and the Al gate are shown. D) SEM image of the gold nanowire.
The aluminum layer is oxidized in air to form 2-3 nm thick insulating surface. Then 100 nm long and 10 nm tall gold nanowires are patterned on the gate. The chip preparation process is demonstrated in figure 5.

1.6. Atomic Force Microscope

AFM stands for Atomic Force Microscopy or Atomic Force Microscope and is often called the "Eye of Nanotechnology". AFM also referred to as SPM or Scanning Probe Microscopy, is a high-resolution imaging technique that can resolve features as small as an atomic lattice in the real space. It allows researchers to observe and manipulate molecular and atomic level features.

![Figure 6: Working principle of AFM in contact mode.](image)
Working principal of AFM is illustrated in the figure 6. AFM works by bringing a cantilever tip in contact with the surface to be imaged. An ionic repulsive force from the surface applied to the tip bends the cantilever upwards. The amount of bending, measured by a laser spot reflected on to a split photo detector, can be used to calculate the force. By keeping the force constant while scanning the tip across the surface, the vertical movement of the tip follows the surface profile and is recorded as the surface topography by the AFM.

The predecessor of AFM is STM, Scanning Tunneling Microscopy or the Scanning Tunneling Microscope, was invented in 1981 by G. Binnig and H. Rohrer who shared the 1986 Nobel Prize in Physics for their invention. Although an excellent technique, STM is limited to imaging conducting surfaces.

AFM has much broader potential and application because it can be used for imaging any conducting or non-conducting surface. The number of applications for AFM has exploded since it was invented in 1986 and now encompasses many fields of nanoscience and nanotechnology. It provides the ability to view and understand events as they occur at the molecular level which will increase our understanding of how systems work and lead to new discoveries in many fields. These include life science, materials science, electrochemistry, polymer science, biophysics, nanotechnology, and biotechnology.

AFM has a number of advantages over other techniques that make it a favorite among leading researchers. It provides easily achievable high-resolution and three-dimensional
information in real space with little sample preparation for low-cost. *In-situ* observations, imaging in fluids, temperature and environmental controls are all available.

The AFM technique has been greatly improved over the past decade. A number of imaging modes have been developed for various applications.

### 1.6.1. Tapping Mode

![Figure 7: Working principle of tapping mode AFM where the cantilever and tip keep on vibrating at a certain frequency and map the surface from the variation of amplitude.](image)

In tapping [acoustic AC] mode: a) a transducer attached to a cantilever housing is used to excite a cantilever into oscillation; b) the amplitude of oscillation when the tip is far from the surface; c) reduced amplitude as the tip approaches the surface.

Contact mode AFM often has a disadvantage for samples that are either weakly bound or soft because the tip can simply move or damage the surface feature and the resulting images are generally not high resolution. The advent of AC mode AFM, which operates in the intermittent contact regime or in the non-contact regime, provides a solution to this problem.
In tapping mode, the cantilever nears its resonant frequency. Tapping or AC mode AFM can be classified into two categories, intermittent contact mode and non-contact mode, depending on the force regime and the tip-sample separation distance. The interaction between the tip and the sample is predominately vertical, thus negligible lateral forces are encountered. Consequently, AC mode AFM does not suffer from the tip or sample degradation effects that are sometimes observed after many scans in contact mode AFM, and it is a technique for imaging soft samples. In AC mode, tip-sample force interactions cause changes in amplitude, phase and the resonance frequency of the oscillating cantilever. The spatial variation of the change can be presented in height (topography) or interaction (amplitude or phase) images that can be collected simultaneously. The system monitors the resonant frequency or amplitude of the cantilever and keeps it constant by a feedback circuit that moves the scanner up and down. The motion of the scanner at each probe location is used to generate a topographic data set. The amplitude change at each probe location forms the amplitude image. The phase data is the result of the phase lag between the AC drive input and the cantilever oscillation output at each probe location. Consequently, contrast in phase images, which are due to differences in material properties, can provide very useful information. In addition, fine morphological features are easily observed in amplitude and phase images.

1.6.2. Gold Mica Substrates

Imaging nanoparticle and molecules which are 1-5 nm in size requires very flat surface with roughness of one tenth of nm or better. High purity gold is epitaxially grown onto
green mica in a high vacuum to prepare atomically flat surface. This surface is perfect for imaging nano materials. The resulting gold surface is 1500 angstroms thick and composed of flat Au (111) terraces up to 280,000 nm$^2$. These substrates were bought from Molecular Imaging and were used as received. To improve the flatness I have tried annealing it in farness in inert atmosphere, but the improvement was little. Moreover it caused bobble formation on the surface may be because of overheated mica. Figure 8 is showing e-beam evaporated gild surface on mica with grain size of $\sim$25 nm. So resolving anything smaller that 25 nm is not possible.

![AFM image of E-beam evaporated gold surface on mica](image)

Figure 8: AFM image of E-beam evaporated gold surface on mica
Epitaxially grown gold on green mica with approximately 500×500 nm² flat terrace is shown in figure 9A. From the scope trace we can observe that the flat terrace has roughness of one tenth of a nanometer.
CHAPTER 2
POLYOXOMETALATE MOLECULAR MAGNET

2.1. Chemical Structure

[PMo\textsubscript{12}O\textsubscript{40}(VO)\textsubscript{2}]\textsuperscript{9-}[1] (figure 10) a polyoxometalate[2] which consists of a central mixed-valence core based on the [PMo\textsubscript{12}O\textsubscript{40}] Keggin [3] unit, able to act as an electron reservoir accommodating a variable number of delocalized electrons hopping over the Mo centers, capped by two vanadyl groups containing two localized spins. The spins on these two (VO\textsuperscript{2+}) units in general are weakly magnetically coupled via the delocalized electrons of the central core. The size (diameter) of the molecule is around 1 nm.

Figure 10: Ball-and-stick model of the polyoxometalate: O (grey), Mo (blue), V (red), and P (yellow).
2.2. Sample Preparation

To deposit the molecules on the substrate they need to be in a solution of suitable solvent and concentration. Polyoxometalate molecules were received in crystalline form. These magnetic molecules oxidize very quickly in air, so to prevent the molecules from degradation they are stored in N₂. All process of solution preparation and deposition of the molecules by self assembly were carried in N₂ environment in a homemade glove box. Deoxygenated water was chosen as solvent as the molecules dissolved in warm water. N₂ was flown through deionized water for 30 minutes to get rid of dissolved O₂. 0.2 mg of microcrystalline powder was added to 20 ml of freshly prepared deoxygenated water and warmed to 50º C. The resulting solution was of concentration ~ 0.1 mMol. Several pieces of gold-mica substrate were then dipped onto the solution to self-assemble the molecules and take out at different time interval to compare the effect of deposition time on self-assembly process. Right after taking out from the solution the substrate was blow dried in N₂ to minimize the surface tension effect. Once the samples were ready then AFM images were taken. Each sample was imaged at several different areas to ensure uniformity.
2.3. Data

2.3.1. Deposited for 5 Minutes

Figure 11: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 5 minutes. (b) Scope trace of the image showing height of the molecules.
2.3.2. Deposited for 11 Minutes

Figure 12: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 11 minutes. (b) Scope trace of the image showing height of the molecules.
2.3.3. Deposited for 38 minutes

Figure 13: (a) AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 38 minutes. (b) Scope trace of the image showing height of the molecules.
2.3.4. Deposited for 60 minutes

Figure 14: AFM Image of polyoxometalate magnetic molecules on gold-mica surface deposited for 60 minutes.

2.4. Discussion

From the AFM image analysis we observe that when assembled for 5 minutes individual molecules are distinguishable without significant layer formation. It was also confirmed by the scope trace height profile. From the height profile of individual molecules we can also find the average diameter of the molecules to be ~0.9 nm. And it agrees very well with the chemical structure of polyoxometalate. When the deposition time was increased to 11 minutes still there were mostly individual molecules with higher surface density. When deposition time was 38 minutes, most of the gold surface was covered by a monolayer of molecules. At this point we could conclude that as the deposition time was
increased the coverage of the gold surface by molecules also increased and with 38 minutes nearly reached monolayer which is desired. So, to get a monolayer 60 minutes of deposition time was allowed and the result was monolayer of molecules on the gold surface with some molecules on the first layer and very small amount of uncovered surface. To be able to measure properties of an individual molecule it is very important to get a monolayer of the the molecules on the substrate. From our study of time dependant deposition we can conclude by depositing from solution of 0.1 mMol concentration for 55-60 minutes we can get a monolayer of molecules suitable for SET experiments.

2.5. Preliminary SET Studies

We have measure the polyoxometalate molecules in the transistor geometry. First the molecules from the deoxygenated and deionizer water were deposited on the chip with gold nanowires by self-assembly. To carry this process the chip was dipped in the solution with the molecules and kept there for 60 mins to get a monolayer on the gold nanowires. The chip was placed in a He³ cryostat and cool down to 4 K. The wires were broken at low temperature to get small gaps. To measure a single molecule we need a gap of the order of the diameter of the molecule. Approximately 150 nanowires were broken at 4 K, typical resistance was 300 ohms at low temperature, with an average break voltage of 0.97 volts and an average breaking current of 2.72 milliamps.
Figure 15: (a) Breaking voltage and (b) current of nanowires as a function of low temperature resistance.

Figure 16: Typical breaking curve for a 10 nm tall 100 nm wide gold nanowire for this data set.

The statistics of electromigration-breaking showed that the majority of wires (nearly half) were completely broken during the process. Figure 17 contains typical post-electromigration states of the nanoscale gaps.
Figure 17: (a) Coulomb Blockade, the current goes to zero near zero S-D bias. (b) STP where we see steps in the conduction near zero bias indicating we may be near a changing charge state of the molecule. (c) SMT where we see an asymmetric curve about zero bias.

NC stands for non-conducting, ZBE stands for zero bias enhancement (non-ohmic), CB stands for coulomb blockade, STP stands for a measurement where we see conductance steps, and SMT stands for some asymmetric tunneling curve that doesn’t pass through zero current. A summary of the post-electromigration conduction through the nano-gap after self-assembling of polyoxometalate molecules can be observed in Figure 18 in wires broken at 4 K.
We found a few broken wires showing discrete steps in the conductance response. However no gate dependence was observed, with the exception of one molecule which was lost after a few measurements. The conclusion is that the molecule should be functionalized with ligands (such as carboxilate groups) to increase the size of the molecule and, thus, increase the chances to bridge the gap in the SET device.
Chapter 3
Mn$_{12}$-Acetate Single Molecule Magnet:

3.1. Chemical Structure

Mn$_{12}$-acetate [Mn$_{12}$O$_{12}$(O$_2$CR)$_{16}$(H$_2$O)$_4$] has been synthesized and reported in 1980 by Lis (1980). In our case R =Me$_3$CH$_2$ which is a derivative of Mn$_{12}$ molecule known as Bu$^-$-acetate. This particular derivative has weaker coupling to the Au electrode. Figure 19 shows a ball and stick model of the molecular structure including only some organic ligands. No water of crystallization and acetic acid molecules are included, although they may play an important role, in particular for the process of tunneling of the magnetization. The inner four Mn atoms which are in the charge state Mn$^{4+} \, (s = 3/2)$
form, together with four O atoms, a (slightly distorted) cube. The eight outer Mn atoms are in the Mn$^{3+}$ ($s = 2$) charge state. The inner Mn ions are coupled antiferromagnetically to the outer ones, yielding a ferrimagnetic ground state with a total spin $S = 8 \times 2 - 4/3 \times 2 = 10$. An evidence of the $S = 10$ ground state has been obtained from high field magnetization studies. There are lots of interests and efforts to study Mn$_{12}$ out of its natural crystalline environment by for example depositing the molecule in different surfaces. However, the Mn$_{12}$ molecules tend to degrade and lose particular properties when taken out of their natural environment, that they poses when in crystal form.

3.2. Sample Preparation

To deposit the molecules on the substrate they need to be in a solution of suitable solvent and concentration. Mn$_{12}$-acetate molecules were received in crystalline form. 2 mg of microcrystalline molecule was added to 10 ml of dichloromethane (CH$_2$Cl$_2$) and stirred gently. The resulting solution was of concentration ~ 2 mMol. Several pieces of gold-mica substrates were then dipped onto the solution to self-assemble the molecules and taken out at different time intervals to compare the effect of deposition time on self-assembly process. Right after taking out from the solution the substrate was blow dried in N$_2$ to minimize the surface tension effect. Once the samples were ready, AFM images were taken. Each sample was imaged at several different areas to ensure uniformity.
3.3. Data

3.3.1. Deposited for 6 minutes

Figure 20: (a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 6 minutes. (b) Scope trace of the image showing height of the molecules
3.3.2. Deposited for 10 Minutes

Figure 21: (a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 10 minutes. (b) Scope trace of the image showing height of the molecules.
3.3.3. Deposited for 20 Minutes

Figure 22: (a) AFM Image of Mn$_{12}$-acetate magnetic molecules on gold-mica surface deposited for 20 minutes. (b) Scope trace of the image showing height of the molecules.
3.3.4. Deposited for 32 Minutes

Figure 23: (a) AFM Image of Mn_{12}-acetate magnetic molecules on gold-mica surface deposited for 32 minutes. (b) Scope trace of the image showing height of the molecules.
3.3.5. Deposited for 47 Minutes

Figure 24: (a) AFM Image of Mn_{12}-acetate magnetic molecules on gold-mica surface deposited for 47 minutes. (b) Scope trace of the image showing height of the molecules.
3.4. Discussion

From the AFM image analysis we observe that when assembled for 6 minutes individual molecules are distinguishable without significant layer formation. It was also confirmed by the scope trace height profile. From the height profile of individual molecules we can also find the average diameter of the molecules to be $\sim 1.5$ nm. And it agrees very well with the chemical structure of Mn$_{12}$-acetate. When the deposition time was increased to 10 minutes still there were mostly individual molecules with higher surface density. When deposited time was 20 minutes 30% of the gold surface was covered by monolayer of molecules. At this point we can conclude that as the deposition time was increased the coverage of the gold surface by molecules also increased and with 32 minutes 85% gold surface covered with monolayer. So to get a monolayer 47 minutes of deposition time was allowed and the result was a monolayer of molecules on the gold surface with some molecules on top of the first layer and very small amount of uncovered surface. To be able to measure properties of an individual molecule it is very important to get a monolayer of molecules on the substrate. From our time dependant study we can conclude that by depositing from solution of 2 mMol concentration for 40-43 minutes, we can get a monolayer of Mn$_{12}$ molecules suitable for SET experiments.
3.5. Preliminary SET Studies

We have measured the Mn$_{12}$-acetate molecules in the transistor geometry. First the molecules from dichloromethane solution were deposited on the chip with nanowires by self-assembly. To carry this process the chip was dipped in the solution of molecules and kept there for 42 minutes to get a monolayer on the gold nanowires. The chip was placed in a He$^3$ cryostat and cool down to 4 K. The wires were broken at low temperature at to get smaller gap. To measure a single molecule we need a gap of the order of the diameter of the molecule. Approximately 90 nanowires we broken at 4 K, typical pre-braking resistance was 250 ohms at low temperature, with an average break voltage of 1.1 volts and an average breaking current of 4.1 milliamps.

We found two wires after breaking show conduction with gate dependence steps.

![I-V curves of single or multiple molecules for different gate voltages (device-I)](image)

Figure 25: I-V curves of single or multiple molecules for different gate voltages (device-I)
This may be results of trapped single or multiple molecules in the nanogap. Figure 25 shows coulomb blockade and the characteristic conduction for different gate voltages in device-I. The differential conductance $dI/dV$ is presented as a function of bias and gate voltages for device-I in figure 26. Discrete steps are observed whenever a new excited state is accessible for conduction. It follows the characteristic diamond structure representative of Coulomb blockade. The $dI/dV$ plot also reveals the level structure of the molecule and thus constitutes a powerful spectroscopy technique to study the energy landscape.
Figure 27: $dI/dV$ as function of bias and gate voltage in a contour plot (Device-II).

Figure 27 presents the data for the second device. This project is ongoing and the preliminary data taken so far is very promising.
4.1. Introduction

While depositing Mn$_{12}$-acetate on the gold-mica substrate from dichloromethane solution, a very strange behavior of the molecule was observed. Most of the time the molecules arranged themselves on the gold surface and if deposited for enough time they form a monolayer and then bilayer and so on. But for this derivative of Mn$_{12}$-acetate for some depositions in some area of the gold substrate the molecules arranged themselves in ring shape structures of different height and diameter as shown in figure 28 and 31. The diameter of the rings mostly varies from 100 nm to 600 nm, though some of them are as large as 1.4 $\mu$m. These rings were first noticed while the molecules were deposited for 30 minutes from three days old solution for initial study. Some area of the substrate was covered with molecules not forming any regular structures. But in some other area of the substrate they form rings. The same type of ring formation was also found in another gold substrate where molecules were deposited for 6 minutes from fresh solution.
4.2. Three Days Old Solution (30 Minutes Deposition)

4.2.1 Data

(a) [Image]

(b) [Image]

Digital Instruments NanoScope
Scan size: 10.00 μm
Scan rate: 1.00 Hz
Number of samples: 512
Image Data: Height
Data scale: 50.00 nm
Figure 28: AFM image of molecules on gold-mica substrate deposited from three day old solution in different areas (a, b, c) showing ring formation.

Figure 29: Diameter distribution of the Mn$_{12}$-acetate rings deposited from three day old solution.
4.2.2 Discussion

From AFM images we observed uniform distribution of Mn$_{12}$ nano rings through the substrate. The diameter distribution of the show that most of the rings are of diameter close to around 150 nm and only very few are 600 nm. The exact reason this behavior is not yet known. To confirm that the nano rings are indeed formed by Mn$_{12}$-acetate we analyzed the height data of the shorter (smaller height) nano-rings. Figure 30 shows the height distribution of the nano-rings. Closely observing the histogram we noticed that the distribution is not continuous and seems to follow a periodic nature, with a 1.6 nm period is a good indication that Mn$_{12}$ molecules are the unit building blocks of the rings. Further detail study is required to reach any concrete conclusion.

Figure 30: Height distribution of the Mn$_{12}$-acetate rings deposited from three day old solution.
4.3. Fresh Solution (6 Minutes Deposition)

4.3.1. Data

(a)

(b)
Figure 31: AFM image of molecules on gold-mica substrate deposited from fresh solution in different areas (a, b, c) showing ring formation.

Figure 32: Height distribution of the Mn$_{12}$-acetate rings deposited from fresh solution.
4.3.2 Discussion

After noticing rings in three days old sample we thought that the rings may form as the solution ages. But as shown in Figure 31, rings are also observed from fresh made solution deposited for 6 minutes. The rings density in this substrate is lower than in the 30 minutes deposition one, which is reasonable. Figures 33 and 34 show three dimensional presentation of the AFM images of deposited from three day old solution and deposited from fresh solution respectively. We notice that the structures are cylinder rather than rings. So the molecules keep piling on top of the other rather than lying directly on the gold surface. We want to further investigate the molecular ring formation since it might allow the fabrication of single molecular magnet based devices.

Figure 33: 3D presentation of the AFM image of molecules on gold-mica substrate deposited from three day old solution (Figure. 28c).
Figure 34: 3D presentation of the AFM image of molecules on gold-mica substrate deposited from fresh solution (Figure. 29c).
5.1. Description

Figure 35: The structure of functionalized gold nanoparticle is represented by a stacking model of red balls. The capping molecules are also shown using a ‘ball–stick’ model: hydrogen (white), carbon (grey), nitrogen (blue), oxygen (green) and sulfur (yellow).

Gold nanoparticles stabilized by means of a surfactant, i.e., weak interaction between protective molecules and Gold surface atoms, are diamagnetic, as bulk Gold samples. It has been also shown that in Gold nanoparticles capped with strong interacting thiols, the number of holes in the 5$d$ band increases resulting in an induced ferromagnetic response. The apparent ferromagnetism is associated with 5$d$ localized holes generated through Au-S bonds [29]. These holes give rise to localized magnetic moments that are frozen in due nanoparticles the combination of the high spin-orbit coupling (1.5 eV) of gold and the symmetry reduction associated with two types of bonding: Au-Au and Au-S. In thiol-
capped Au NPs the counterbalance between size effect and ligand effect tunes the structure and total number of $d$ holes. Since magnetic behavior is determined by the $d$ electrons, it is expected that the magnetic properties can be also tuned upon different capping and size. It should be remarked that nanosized particles holding permanent magnetic moment play a key role for the basic understanding of magnetism as well as for miniaturized data-storage technology [30] and may reveal novel application in energy nanotechnology. Our interest is on the study and understanding of the capping induced ferromagnetism at the individual nanoparticle level. For this, transport studies in individual gold nanoparticles with the use of single-electron transistor devices are among our immediate objectives.

Crucial for the study of electrical transport through individual particles in a SET device is a controlled and homogeneous deposition of the particles in atomically flat surfaces, which sets the focus of the study presented in this section of the thesis.

5.2. Sample Preparation

To deposit the gold nanoparticle on the substrate they need to be in a colloidal solution of suitable solvent and concentration. Gold nanoparticles were received in concentrated colloidal solution in toluene. Then more solvent was added to dilute the stock solution. For getting a monolayer of nanoparticles choosing the right concentration is very important. To find proper concentration several diluted solutions were prepared and gold nanoparticles deposited on gold-mica substrate for 5 minutes and imaged. Figure 36 shows images of nanoparticles deposited from 1:25 and 1:50 diluted solution. It is clearly
visible that with these concentration nanoparticles are not forming a uniform layer. So a further diluted solution (1:100) was used to get slower and more uniform deposition. Several pieces of gold-mica substrate were then dipped onto the solution to self-assemble the nanoparticles and taken out at different time intervals to compare the effect of deposition time on self-assembly process. Right after taking out of the solution it was blow dried in N$_2$ to minimize the surface tension effect. Once the samples were ready then AFM images were taken. Each sample was imaged at several different areas to ensure uniformity.

Figure 36 AFM images of nanoparticles deposited from (a) 1:25 and (b) 1:50 diluted solution

47
5.3. Data

5.3.1. Deposited for 16 Minutes

Figure 37: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 16 minutes.
5.3.2. Deposited for 37 Minutes

Figure 38: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 37 minutes.

5.3.3. Deposited for 64 minutes

Figure 39: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 64 minutes.
5.3.4 Deposited for 400 Minutes

Figure 40: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 400 minutes.

5.3.5 Deposited for 1100 Minutes

Figure 41: AFM Image of magnetic gold nanoparticle dilution 1:100, on gold-mica surface deposited for 1100 minutes
5.4. Discussion

From the AFM image analysis we observe that when assembled for 16 minutes individual molecules are distinguishable without significant layer formation. It was also confirmed by the scope trace height profile. From the height distribution of individual nanoparticles we can also find the average diameter of the molecules to be 2.6 nm, with a Gaussian distribution width of 1.46 nm (see figure 42). This result agrees with the average diameter extracted from optical characterization (plasmonic resonance).

When the deposition time was increased to 37 minutes still there were mostly individual molecules with higher surface density. The results of deposition for 64 were similar to that of 37 minutes but the individual nanoparticles stated to form clusters.

Figure 42: Height distribution of the magnetic gold nanoparticles deposited from 1:100 diluted solution.
To get a uniform coverage of the surface we next tried 400 minutes. The results show that over 60% of the gold mica-surface was covered with gold nanoparticles with some larger cluster. It was evident from these studies as the deposition time increases assembly process become slower. So to get a monolayer 1100 minutes of deposition time was allowed and the result was a monolayer of molecules on the gold surface with some clusters of molecules on top of first layer. The cluster formation seemed to be unavoidable at this concentration. One was could be to use lower concentration colloidal solution. But in that case the deposition time to get a monolayer of nanoparticles will be considerably higher. To be able to measure properties of an individual molecule it is very important to get a monolayer of the coverage. From our study of time dependant deposition and taking, concentration and deposition time in to account the best case scenario is to deposit from 1:100 diluted solution for 1000 minutes.

Single-electron transport measurements are planned to be initiated within the following weeks during the Summer 2008 semester.
I have developed a controlled way of depositing a uniform monolayer of molecules/nanoparticles on atomically-flat gold surfaces. The final goal of these studies is to prepare single-electron transistors using gold nano-electrodes. The deposited layer of nano-material on gold substrate was extensively examined using AFM image analysis. I have studied three different magnetic nano-materials (i) a molecular magnet; (ii) Mn$_{12}$-acetate: a single-molecule magnet; (iii) a functionalized magnetic gold nanoparticle. From these studies I conclude that:

(1) The average diameter of the polyoxometalate molecules is $\sim$0.9 nm, which evidences the preservation of the molecule when deposited in the substrate. The analysis resolves that deposition from 0.1 mMol concentration solution for 60 minutes would form a monolayer on gold surface.

(2) The average diameter of the Mn$_{12}$-acetate molecules is $\sim$ 1.5 nm, which agrees with diameter expected for this molecule and reveals that the Mn12 core remains intact after the deposition. I found that depositing from a solution of 2 mMol concentration for 40-43 minutes would form a monolayer on gold surface.

(3) The average diameter of the gold nanoparticles is 2.6 nm, in agreement with diameter extracted from optical spectroscopy. I found that a 1:1000 diluted solution and depositing for 1100 minutes would result a monolayer of particles on gold surface.
The size of the molecules and nanoparticles agrees well with results from chemical and optical studies. The preliminary electrical transport measurements also indicate that using the concentrations and deposition times mentioned above increases the probability of measuring individual nanoparticles or nanoscale molecules, which is of great interest due to their potential future application in nano-electronics.

We have also observed interesting behavior of Mn$_{12}$-acetate molecules as they form nano-rings. These nano-rings have periodic height of 1.6 nm, which nearly equal to the diameter of the Mn$_{12}$ molecules, a good indication that Mn$_{12}$ is the unit building block of the nano-rings.
LIST OF REFERENCES

[1] Q. Chen and C. L. Hill, *A Bivanadyl Capped, Highly Reduced Keggin Polyanion, [PMoV\textsubscript{6}Mo\textsuperscript{VI}\textsubscript{6}O\textsubscript{40}(\textsuperscript{VI}O)\textsubscript{2}]\textsuperscript{5-},* Inorg. Chem. 35, 2403 (1996).


