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ENTITLED: Preparation of Gold(III) and Dichalcogenide AFM/STM Substrates

and Underpotential Deposition Studies of Lead on Silver(III)

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

College of Liberal Arts and Sciences

Instructor in Charge

APPROVED: 

HEAD OF DEPARTMENT OF Chemistry
Preparation of Gold(111) and Dichalcogenide AFM/STM Substrates

and

Underpotential Deposition Studies

of Lead on Silver(111)

By

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Thesis for the

Degree of Bachelor of Science

in Chemistry

College of Liberal Arts and Sciences

University of Illinois

Urbana, Illinois

1991
Acknowledgements

I would like to thank everyone here who has encouraged me to endeavor for the advancement of knowledge, but especially those who have assisted me with this work.

I am particularly indebted to the members of my research group whose invaluable advice and friendship have helped strengthen my dedication to continuing research. Thanks to Bradnon Chuickshank and Dougie Sneddon, T.A. for their expertise and enlightenment on the techniques of STM. Thanks to Dawn Sabel and Scott Clingman for providing a jovial atmosphere in which to do research, and for fresh fluffy pancakes. I would especially like to thank Mr. Chun-hsien Chen, not only for his time and advice on the many matters of electrochemistry and AFM, but also for showing me the value of persistence and dedication to one’s work.

Thanks to Emman Ramli and Jerome Hubacek for sharing their knowledge of vapor transport crystal growth. Thanks also to Bryan Parker, Sparky Meyers, and Dr. Andy Gellman for their advice and materials for crystal polishing. I also thank Dr. Jeff Forbes for his suggestions on vapor deposition.

I also would like to acknowledge the National Science Foundation’s Research Experience for Undergraduates program, run through MRL, for their partial support of this work.
Finally, my no-holds-barred gratitude goes to Dr. Andy Gewirth for allowing me the freedom to learn on my own, but at the same time have him as a guru and egghead-pundit in doing this work.
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Abstract

There were several stages to this research project, but all had the common goal of the preparation and study of various metallic substrates using atomic force microscopy (AFM) and/or scanning tunneling microscopy (STM). First, several molybdenum, tungsten, and platinum dichalcogenides were grown as large crystals (5-15 mm²) by means of iodine vapor transport. The starting materials were sealed in quartz ampoules and subjected to fixed temperature gradients for many days to produce large crystals of suitable size for study with STM or AFM.

Next, research was done to find a practical method for the epitaxial growth of gold(111) onto cleaved mica substrates. Among the more important factors controlling epitaxial growth are: vacuum pressure, substrate temperature, rate of deposition, and distance from the vapor source to the mica surface.

Continuing along this line, a procedure for the mechanical and chemical polishing of a silver(111) single crystal was investigated. Although the chemical finishing polish may be varied and still give comparable results, it was difficult to mechanically polish the crystal initially to the point where it consisted of large, nearly atomically smooth silver islands.

With the crystal as smooth as possible, underpotential deposition (UPD) studies of lead onto the silver(111) surface were performed using varying electrolytes, including perchlorate, acetate, and citrate. Based on the
correlation of the surface under different potentials, several hypotheses may be made as to the nature of the electrochemical growth mode of lead on silver. Various factors appear to play a role in the UPD process. Among them are the quality of the silver(111) surface, the parameters for running the cyclic voltammograms, and either complexation or adsorption of various anions.
There are many reasons why transition metal dichalcogenides are intrinsically interesting to study. Many such compounds, such as PtS₂, crystallize in a lamellar structure, with adjacent layers weakly held together by van der Waals forces. As a result of its layered-type structure, PtS₂ shows promise as an excellent semiconductor because charge transfer occurs from platinum to sulfur, which results in a gap between the d bands of platinum, and thus the compound's semiconducting properties. As another example, by changing the chalcogens bound to platinum, PtS₂ is a semiconductor, PtSe₂ is a semimetal, and PtTe₂ is a true metal with a complex Fermi surface.

Molybdenum and tungsten disulfides show promise as lubricants and lubricant additives due to their layered structures. MoSe₂, WS₂, and WSe₂ may also form the basis for a new class of electrodes for electrochemical solar cells, and as stable, efficient photoelectrodes. Molybdenum dichalcogenides have also been used as active cathodes in lithium batteries. The structural makeup of these materials, either crystalline or amorphous, is of critical importance in the reactivity of these compounds. As an example, only the crystalline compound MoS₂ is able to intercalate lithium. By varying the stoichiometries of molybdenum to sulfur from 1:2 to 1:3, the compounds show different reactivities and degrees of intercalation of foreign atoms. In the case of the lithium battery, varying the stoichiometries by only a few
substrates is all of the properties discussed for these transition metal dichalcogenides is the necessity of having a well-defined surface. The electrochemical, photochemical, and lubricating properties of these compounds are strongly dependent on various surface characteristics. The study of these materials by STM and/or AFM is ideally suited to understanding both the long-range (several microns) as well as atomic level features of these surfaces. By gaining knowledge of the surface features and related electronic interactions of these transition metal dichalcogenides, the important electronic and structural features of these compounds may be controlled and used for practical applications.

The main thrust of this research project deals with the preparation and electrochemical characterization of gold(111) and silver(111) single crystal substrates. For many STM/AFM experiments it is desirable to have an atomically flat surface to allow for optimum conditions for imaging and spectroscopy of adsorbed atoms, molecules and biological structures.7 These substrates are also ideal for physically induced high resolution surface modification for microscopic dynamics studies, lithographic purposes, and most important to our studies, surface electrochemistry.8

Unfortunately, even though single crystal surfaces are ideal for many different types of surface studies, they are difficult to prepare and maintain in ideal condition. In the case of the gold substrate, the surface was prepared by epitaxially depositing gold onto freshly cleaved mica inside of a
bell jar evaporator. No matter how carefully the conditions are controlled during the deposition process, there are always limits to the long range order of the metal surface due to steps, mosaic structure, and strain parallel to the surface.

Eventually, a complete, reproducible procedure was discovered for the epitaxial deposition of gold onto mica. It was first necessary to obtain a consistent vacuum of ca. 10^{-6} Torr. Then, it was essential to find a method of uniformly cleaving each of the individually cleaved mica pieces, because thermal effects due to uneven heating can cause non-epitaxial growth, as well as a lack of atomically smooth regions. Other factors playing roles in controlling the quality of surfaces grown on the mica were: vapor source to sample distance, rate of evaporation, preheating and temperature of the mica, and surface contamination.

Underpotential deposition is defined as the deposition of a monolayer amount of metal atoms onto a foreign metal surface at electrode potentials positive with respect to the reversible Nernst potential. Research in this group has been intently focused on two underpotential deposition processes (UPD). The first is the UPD of silver onto gold(111), and the other being the UPD of lead onto silver(111), which is detailed in this paper.

Unlike the case of the gold, the vapor deposition of silver onto mica met with limited success due to oxidation of the metal upon removal from the bell jar evaporator. Instead, a procedure was followed for the mechanical and chemical polishing of a silver(111) single crystal.
Atomic Force Microscopy (AFM) is well suited for the study of electrochemical processes such as UPD. AFM provides structural information as to the nature of surface species and their packing arrays. At the same time, AFM is relatively uninhibited by the harsh chemical environments and the electronic perturbations of the system of study.

There are several factors which control the UPD of lead onto silver. As UPD is entirely a two dimensional phenomenon, the flatness of the surface is obviously critical to obtaining the growth of a monolayer. The orientation of the substrate metal surface, for example, Ag(111), (110), or (100), partly defines how well the monolayer deposition is either facilitated or inhibited. The difference in size and preferred packing orientation between the substrate atoms and the adatoms is also important, as it determines whether or not the monolayer may pack commensurately with the surface.

Other than the compatibility of the surface geometries of the two interacting species, the other equally important factor in controlling the UPD process is the nature of the supporting electrolyte. Certain organic anions, such as acetate and citrate, have strong adsorbing properties which tend to interfere with the bonding between the adatom and the surface. These same anions may also interfere with the UPD process by directly attacking the lead cation, resulting in bulky complex formation, and thus the inability of the adatom to bond with the surface. Also, at a certain concentration of lead, usually ca. 10^{-2} M, there is a crossover from diffusion control to nucleation control of the UPD process. Usually, below this concentration the process is diffusion controlled and thus independent of the anions.
present. And above this concentration, the process is more of a nucleation phenomenon, in which the anions present have a much greater impact.

The other major factor which controls the UPD process is the electrochemical cycling of the system. Although UPD is generally accepted to follow an instantaneous nucleation and growth model\textsuperscript{16}, the actual mechanism is far from ideal, due to several aforementioned factors. The reversibility of the process, and the hysteresis between the underpotential deposition (UPD) and underpotential stripping (UPS) peaks is strongly correlated to the voltage sweep rate.\textsuperscript{17} Since the process is not truly instantaneous, applying too fast of a sweep rate will not allow time for all of the nucleation and growth processes to occur before the cycle is reversed. The UPD process may also be affected by electrochemically cleaning the surface. In reality, the instantaneous nucleation does not occur evenly across the surface, but instead occurs preferentially at cleavage steps, or adsorbed impurities. Thus, the surface can be cleaned of these impurities by holding the potential of the system at some highly anodic point. This in turn provides fewer sites for nucleation, and therefore causes the monolayer deposition to occur at a much slower rate. On the other hand, the system may also be held at some highly cathodic (negative) potential in the region of bulk lead deposition. Thus when the system is cycled back to an anodic potential, past the stripping peaks of lead, some of the lead will still remain on the surface. These remaining lead sites will provide additional nucleation sites for lead atoms during the cathodic sweep, and this in turn will cause the UPD process to occur faster and more completely.\textsuperscript{16}
Within this paper is described many of the experimental conditions and procedures for the synthesis of various STM/AFM substrates. Also included is the detailed investigation of the many factors governing UPD of lead onto silver(111). Although many questions are left unanswered as to the nature of the UPD process, many insights and ideas have been gained through this research.
Experimental

I. Transition Metal Dichalcogenides

A. Materials and Equipment

Doubly sublimed iodine (Fisher, 99.8%), WSe\textsubscript{2} (ROC/RIC, 99.9%), WS\textsubscript{2} (ROC/RIC, 94.8%, 1-2 micron powder), and MoS\textsubscript{2} (powder) were used as indicated. Quartz ampoules were fabricated by the School of Chemical Sciences Glass Shop (Figure 1). A turbo pump and hydrogen-oxygen torch were used for sealing off the quartz ampoules. Programmable two zone shunt tapped tube furnaces were used for crystal growth. Hydrofluoric acid and aqua regia (2.5:1, HCl:HNO\textsubscript{3}) were used for cleaning the ampoules for reuse, and a 90°C drying oven was used for removing excess water after cleaning.

B. Compounds and Synthetic Procedures

All compounds were prepared by sealing the starting materials with a slight excess of iodine transporting agent inside the ampoules. The quartz ampoules were cooled in liquid nitrogen while being sealed to prevent the sublimation of I\textsubscript{2}. During the process of sealing off the ampoules, the pressure inside was maintained between 10\textsuperscript{-4} to 10\textsuperscript{-5} Torr with the use of a turbo pump. The ampoules were placed in the tube furnaces, with the starting materials at the hot end and the growth zone at the cooler end. Temperatures inside the tube furnace were monitored with the use of a
thermocouple. The temperatures were then programmed and allowed to rise to their respective set points, with the ampoule in place inside the furnace. In removing the ampoules at the end of the growth process, they were either taken out with the ampoule still at its reaction temperature or after allowing it to cool down to 100°C. No difference in crystal quality was noted between these two methods. Opening the ampoules was accomplished by first scoring one-half of the narrow neck region, then covering the scored area with a thick rubber hose and breaking in half.

WSe₂ was synthesized over a ten day period, with the reactants' end at 850°C and the growth zone at 800°C. WS₂ was synthesized over a twenty-one day period, with the reactants' end at 885°C and the growth zone at 720°C. MoS₂ was synthesized over a fifteen day period, with the reactants' end at 820°C and the growth zone at 750°C. Most crystals grown were smooth, lustrous, and platelike, with surface areas of about 5-15 mm².

II. Vapor Deposition of Gold onto Mica

A. Materials and Equipment

The bell jar evaporator (Figure 2) used for depositing gold onto mica is a large, mechanically operated setup, with vacuum pressure achieved by means of a 6 inch diffusion pump, backed by a one horsepower mechanical pump. A good deal of restoration was required to get the bell jar in working
condition. A helium leak detector, Glypt, Torr Seal, and Apiezon grease were instrumental in establishing vacuum pressures in the $10^{-6}$ Torr range.

The interior equipment of the bell jar consists mainly of: a 5 ml tungsten boat used for resistively heating the gold, a movable aluminum shutter which can be placed between the metal source and the substrate, a copper sample holder (Figure 3), a copper-constantane thermocouple, and a crystal thickness monitor. The mica samples were heated by two 150 W filament heaters. The heating efficiency of the sample holder was enhanced by lining the sample holes with indium wire to promote better heat conduction and also by using a reflective aluminum shield to deflect heat back to the samples.

B. Deposition Procedure

Freshly cleaved mica pieces (ca. 0.6 inch diameter) were placed inside the bell jar on the copper sample holder. A reflective aluminum foil shield was placed over the filament heaters to more evenly distribute heat back to the mica pieces. The bell jar was then evacuated to about $2\times10^{-6}$ Torr over the course of at least one hour, with liquid nitrogen added to cool the diffusion pump trap. After reaching the lowest attainable pressure, the filament heaters were turned on to heat the copper plate (and the mica samples) to between 230-250°C. After baking the samples out for 10-15 minutes, or until the pressure stabilized, the deposition was begun.

The variac controlling the gold heater was turned up to ca. 25-30 volts, until the gold became molten. After a short time at this temperature (ca. 10-
20 seconds), the aluminum shutter was moved out of the path between the gold and the mica. The distance between the gold and the mica was normally kept between 14-16 inches. During the gold deposition process, the temperature of the mica substrates was kept at at least the same temperature as it started at. The rate of evaporation of the gold was checked with the crystal thickness monitor and normally varied from 3-5 Å/second, until 1000 Å had been deposited on the mica samples. At this point the deposition was stopped, everything was turned off, and the samples were allowed to cool for about 2 1/2 to 3 hours before removing them.

III. Silver(111) Crystal Polishing Procedure

A. Materials and Procedure: Mechanical Polishing

A silver(111) single crystal (13 mm diameter) was mounted on a circular piece of glass, which was in turn glued to an invar sample holder. The crystal was then mounted in a small macor holder used for keeping the sample in place and flush to the polishing surface during all described polishing procedures. Abrasive materials used for mechanical polishing include: 320 grit emery paper, 400 grit emery paper, nylon cloth, 6 micron diamond paste, 1 micron diamond paste, Buehler microcloths, 0.3 micron alumina, and 0.05 micron alumina.

For all polishing done by hand, the crystal was moved in a linear motion, back and forth, until all visible scratches on the surface of the crystal were
aligned. At this point, the crystal was turned 90°, and the same procedure was repeated. At each stage, polishing was continued until all of the scratches on the Ag(111) crystal were aligned and of uniform width.

Initially, the crystal was polished with 320 grit emery paper under running water for 15-20 minutes. Next, the crystal was polished with 400 grit emery paper, also under running water, for 25-30 minutes. These two hand polishing processes, using emery paper, were never again repeated, as this procedure quickly degrades the thickness of the crystal.

Hand polishing was then continued using 6 micron diamond paste on nylon cloth for ca. 30 minutes. After 30 minutes of polishing with full pressure on the crystal, the procedure was continued for another 60 minutes, still using 6 micron paste, but applying only half pressure. Next, 1 micron diamond paste on nylon cloth was used for 60 minutes, applying full pressure. Finally, hand polishing was completed using 1 micron paste for 90 minutes, again applying only half pressure.

The mechanical polishing procedure was completed using a microcloth mounted on a polishing wheel. While using the polishing wheel, care was taken to ensure that the microcloth used was not frayed. Care was all taken to ensure that the cloth remained wet (not just damp), as the alumina can create large scratches on the crystal if not properly dispersed in solution. Similar to the hand polishing procedure, the crystal was held in a stationary position with the wheel rotating between 180-240 rpm's. The crystal was then kept in place until all scratches were aligned and of similar size. Then the crystal was turned 90°, and the procedure was repeated.
First, polishing was done for 15-20 minutes using 0.3 micron alumina in solution. Next, polishing was completed using 0.05 micron alumina for 10-15 minutes. These last two procedures were repeated several times through the course of experimental runs, especially when chemical polishing was unable to restore the crystal to the condition necessary for future AFM/UPD studies.

B. Chemical Polishing Procedure

A chemical polishing solution was made by dissolving 5.25 g of NaCN and 19.5 g of 30% H_{2}O_{2} in 250 ml of solution. A wash solution was made by dissolving 9.4 g of NaCN in 250 ml of water. After completing the mechanical polishing, the crystal was chemically polished by dipping it into the polish solution for five seconds, holding it in air for five seconds, then dipping it back into the polish solution for an additional one second. The etching action of the polish solution was halted by dipping the crystal into the wash solution until bubble evolution from the surface stopped (usually 2-3 seconds). Finally, the crystal was washed with water and allowed to air dry before performing any electrochemical experiments. This chemical polishing procedure was repeated after every experiment to ensure a clean surface for future experiments.
IV. Electrochemical and AFM Procedures

A. Cyclic Voltammetry: Instrumentation and Methods

Cyclic voltammograms, used for measuring the position and efficiency of the UPD processes, were recorded using a BAS CV-1B potentiostat and a Houston Instrument 2000 chart recorder. The electrochemistry was run either in a teflon cell or in a glass cell with a viton o-ring for doing AFM experiments (Figure 7). The working electrode was always the silver(111) single crystal, and the counter electrode was a platinum wire. In the teflon cell, a Hg/Hg$_2$SO$_4$ reference electrode was generally used. In the AFM glass cell, a silver wire was always used as the reference electrode.

Initially, UPD studies were carried out in the teflon cell, without any connection to the AFM. After establishing the reproducibility of the electrochemistry, the UPD studies were then combined with AFM studies to provide structural information on the UPD process. Three different electrolytes were used to study the UPD of lead onto silver(111).

The first and most extensively studied electrolyte consisted of 10$^{-3}$ M Pb(ClO$_4$)$_2$, 5$\times$10$^{-3}$ M HClO$_4$, and 0.5 M NaClO$_4$. The potential range for UPD studies with this electrolyte went from -0.1 to -0.89 volts with respect to a Hg/Hg$_2$SO$_4$ reference electrode. UPD occurred at ca. -0.71 V and bulk deposition at -0.88 V (Figure 4). The UPD peak was strongly reversible, and the data was easily reproduced in the teflon cell. Upon changing to the glass cell, however, the quality of the UPD peak, or smoothness of deposition,
decayed somewhat. The data was also generally less reproducible than in the teflon cell.

The next electrolyte investigated was: $10^{-3}$ M Pb(CH$_3$COO)$_2$, $10^{-2}$ M CH$_3$COOH, and 0.5 M Na(CH$_3$COO). The potential range studied generally went from -0.2 to -0.96 volts with respect to a Hg/Hg$_2$SO$_4$ reference electrode. UPD occurred at -0.825 V and bulk deposition at -0.955 V (Figure 5). The UPD peak was reversible, though it showed more hysteresis with the stripping peak than the perchlorate solution did. Reproducibility was also poorer than with the first solution. Changing to the glass cell seriously hampered the reliability of the CV data from the UPD process, as the CV's appeared very erratic.

The final electrolyte studied contained: $10^{-3}$ M Pb(CH$_3$COO)$_2$ and 0.5 M Na$_3$C$_4$H$_5$O$_7$. The potential range was -0.22 to -1.08 volts with respect to a Hg/Hg$_2$SO$_4$ reference electrode. UPD occurred at -0.87 V and bulk deposition at -1.07 V (Figure 6). The UPD peak was reversible, but there was some other undefined structure in the interlayer region between the UPD and bulk peaks. The data was not very reproducible, and the system was never tried in the AFM glass cell.

B. AFM: Instrumentation and Methods

For all AFM UPD studies, a Digital Instruments Nanoscope II STM/AFM was used with a short range AFM scan head (ca. 1.1 microns). The electrochemical/AFM cell consisted of the silver(111) single crystal as a base.
a viton o-ring provided the sidewalls, and the AFM glass cell, which provided ports for the other two electrodes (Figure 7). Scanning was done with gold coated Si$_3$N$_4$ Nanoprobe cantilevers. A triple vibration isolation system was used, consisting of a rubber pad placed beneath the microscope, a hanging concrete platform suspended by bunge cords, and a Newport GS-34 vibration isolation lab bench.

The smaller and thinner of the two cantilevers was used for experiments, whereas the larger one was broken off to prevent interference with the collected data. The cantilever was mounted in the AFM glass cell, followed by the placement of a sonicated o-ring in the corresponding groove. The glass cell was then secured to the microscope head, and the assembly was placed over the crystal. Prior to this, the crystal was mounted on the scan head and electronically connected, by means of silver paint, to a wire outside the cell.

With the aid of a 20x scope, the AFM microscope assembly was mechanically lowered to a point just above the Ag(111) surface. Following this, the laser was connected and the beam was aligned onto the tip of the cantilever. The laser alignment was checked by noting a sharp point of light reflected off the tip onto a closely placed piece of paper, and also by noting a horizontal oblong image projected onto the wall behind the diodes. Also, when the laser is properly aligned, a maximal reading is observed on the A+B voltage scale. After laser alignment, the position of the diodes was also adjusted to maximize the A+B reading. The cantilever was then lowered closer to the surface, if necessary, before engaging the tip. All scans were done in the height mode.
Long range images (ca. 1 micron) of the surface were then obtained in air. After the instrument parameters stabilized (mainly the Z range) and real images were observed, the cantilever was slightly withdrawn and the solution was added to the cell. The laser and diodes were then realigned, and the tip was reengaged. After allowing time for thermal stabilization of the system, the UPD experiments were conducted.

In the perchlorate system, the main system of study, both long and short range AFM scans were taken at many points of the deposition/stripping cycle. First, long range images of silver(111) were taken in solution with no potential control. Next, the potential was held at 0 V versus silver wire, and images were recorded. Long and short range scans were likewise recorded at: -0.3, -0.462, -0.549, -0.669, -0.744, and -0.895 volts versus silver wire. This AFM data was then stored for later analysis.

The short range images, where atomic level corrugation was observable, were then processed. By using the zoom box, the regions of the scan that looked to give promising results were separated from some of the extraneous noise and tip drag regions. This data was then lowpass filtered and two dimensionally fourier transformed to give clearer images of the actual spacing between rows and atoms.

Complete AFM data was also collected at a different time, at similar potentials, to provide a basis for comparison and reproducibility.
Results and Discussion

I. Dichalcogenide Crystal Growth

Several types of transition metal dichalcogenides were grown by means of iodine vapor transport, using a sealed quartz ampoule under a fixed temperature gradient. MoS$_2$ crystals were grown only twice, and each attempted growth resulted only in clumping of the crystals in the narrow section of the ampoule. WS$_2$ was repeatedly synthesized, varying both the length of time of growth and the temperature gradient. The time of growth had little impact on the crystal sizes, provided the time was longer than a minimum of about 14 days. The temperature gradient, however, greatly affected the crystal sizes. In general, the smaller the temperature gradient used, the larger the crystals grown—provided the gradient from the reactant zone to the growth zone was greater than about 150$^\circ$C.

WSe$_2$ crystals were also grown multiple times, also varying the time of growth and the temperature gradient. Again, similar effects were found, as in the WS$_2$ crystals, by varying these two parameters. With WSe$_2$, the minimum permissible growth time was about 10 days, and the minimum temperature gradient was about 50$^\circ$C. One change tried that varied from the other growth procedures involved reversing the temperature gradient after 24 hours. With WSe$_2$, if the temperature gradient was not reversed after 24 hours most of the crystals would cluster together in the narrow end of the ampoule. Although not conclusive, reversing the gradient appears to have resulted in higher yield, if not necessarily larger crystals.
Although none of the MoS\textsubscript{2} crystals grown were of suitable size for STM/AFM study, several large (5-15 mm\textsuperscript{2}) WS\textsubscript{2} and WSe\textsubscript{2} crystals were grown. Unfortunately, many of these large crystal platelets were contaminated by starting material or smaller crystals. Often times it was difficult to mount these crystals flat for study because their back faces were clumped with extraneous material. For this reason and because of the difficulty of aligning the STM tip with these small substrates, no images were obtained of the surface structures of these dichalcogenides.

There are several factors which can improve the size and quality of the crystals grown. First, it is necessary to establish as low of a pressure as possible within the ampoule before sealing it. As the temperature is increased during the reaction, the pressure inside rises greatly. By having the lowest possible pressure inside the reaction vessel, more diffusion of the reactants and transporting agent is allowed, and transport occurs at a greater rate. This in turn leads to more growth at nucleation sites, and thus larger crystals.\textsuperscript{17}

Another related way of increasing the quality of the crystals grown is to reverse the temperature gradient after 24 hours, or some other period of time which is small in comparison to the total growth time.\textsuperscript{18} By doing this, the reactants are also allowed to disperse more and in turn grow into larger crystals.

Perhaps the factor which most greatly influences the number and size of the crystals grown is the magnitude of the temperature gradient in the growth zone. With the use of a three zone tube furnace, the temperature can be controlled such that the reactant's end of the ampoule is at a much
greater temperature than the close end of the growth zone. Then, the third zone, at the far end of the growth zone (ca. 1 inch past the near end of the growth zone), may be kept at the same temperature as the near end of the zone (Figure 1). The result of keeping this one inch region of the growth zone at the same temperature is that the crystals may grow evenly throughout this region without clumping at the end of the ampoule.17

Another factor which influences the transport of the materials is the surface area of the starting material.19 By starting with a very fine metal dichalcogenide powder, there is a minimal amount of surface area which can react with the transporting agent. The water adsorbed in the walls of the quartz ampoule has also been found to influence the transport of at least MoS2 and WS2.20 Iodine alone is insufficient to transport these two compounds, because each of these two materials appears to move in the form of an oxide formed by the water present in the quartz glass. Other compounds such as PtS2 and PtTe2 cannot be transported by using halogens, but instead must be reacted with an appropriate mixture of phosphorous and sulfur.21

Finally, one other factor that influences the attainment of usable crystals is the process of opening the ampoules. By breaking the vacuum while the break point is surrounded by a rubber hose18, the pressure inside the ampoule is not increased as rapidly as if the procedure is just done open to air. By slowing the rate of pressure change, the crystals are not jolted as much and are thus less likely to break into smaller, unusable fragments.
II. Gold on Mica AFM Substrates

Gold(111) was epitaxially deposited onto mica inside a bell jar evaporator. Vacuum pressure was maintained between 2-5 x 10⁻⁶ Torr throughout the deposition process. After 11 vapor depositions, the quality of the gold substrates was determined by comparing the oxidation-reduction cycle of the subs. in 0.01 M perchloric acid with the established electrochemistry of gold(111).³¹

Mica substrates were first cleaved with adhesive tape. The pieces were then placed in the holes of the copper plate and heated with two tungsten filament heaters. Several procedures were attempted to heat the mica pieces more evenly. The first change that was made was using two filament heaters instead of one to give more even heating. Steel washers were next placed on top of the mica pieces, both to hold them in place and to increase heat conduction. Lamentably, some outgassing occurred from the washers which disrupted the vapor deposition. Instead, deeper grooves were bored around the sample holes to keep the mica pieces in place while closing and opening the bell jar. The next change made was to use a copper plate instead of the original aluminum sample holder to provide better heat conduction. The holes of the copper plate were then lined with indium wire to further improve heat conduction. Finally, the heater/sample holder assembly was enclosed within an aluminum foil dome to contain more heat within the sample holder area.

Other changes made include heating the mica pieces to ca. 230-250°C before depositing the gold. Originally, the samples were only heated to ca.
190-220° C before beginning the deposition. At other times, temperature ramping of the substrates was tried to improve the epitaxy of the surfaces. In these cases, the temperature of the mica substrates was increased from ca. 240 to 260° C during the course of the deposition. The effect of this was similar to keeping the samples at a constant temperature between 230-250° C, as both methods produced satisfactory gold(111).

Besides staying within the above temperature ranges, of almost equal importance to obtaining good surfaces is preheating the substrates. In general, the mica pieces were baked out for 10-15 minutes before depositing the gold. Without this preheating, the single crystalline quality of the gold was seriously diminished, as evidenced by the cyclic voltammograms.

Although the rate of deposition was normally kept between 3-5 Å per second, this factor appears to have had relatively little influence on the quality of the gold produced. Even deposition rates in excess of 15-20 Å per second produced satisfactory gold(111) single crystal surfaces.

One other factor that was somewhat important was the amount of gold placed inside the tungsten boat. Placing too little gold in the boat resulted in an incomplete deposition because the boat would run dry, but placing too much gold in the boat also resulted in an incomplete deposition. The ideal amount of gold needed for a deposition was about 2-2.5 grams.

Using more gold than this resulted in the gold overflowing from the edges of the boat. This created two problems, one being that this excess gold was no longer subjected to the hottest part of the boat and was thus not vaporized. The other problem was that this excess gold interfered with the heating of the boat by increasing the resistance around it. This factor caused
a couple of the depositions to stop completely, either due to too slow of a rate of gold vaporization or because the brittle tungsten boat was cracked by applying too much voltage over too long of a time.

In general, the standard procedure for growing a suitable gold(111) single crystal substrate inside a bell jar evaporator involves depositing 1000 Å of gold, under a pressure of no greater than $2 \times 10^{-6}$ Torr, with a vapor source to mica distance of at least 10 inches. It has also been found that the higher the rate of deposition, the smoother the film. Smoothness, however, has a different meaning on an atomic scale than it does on a macroscopic or visible scale. Just because a surface does not look smooth does not mean that it will not give a good AFM image or provide a redox cycle evident of a single crystal. The other problem with depositing gold too fast is that some of the molten gold may splatter onto the mica surface, along with the gold vapor, destroying the epitaxy.

The single most important factor to obtaining good epitaxial growth is controlling the mica temperature. Thermal effects due to uneven heating quickly destroy the epitaxy of the gold surface by creating hot and cold spots on the mica, which leads to wavy, uneven surfaces. As the epitaxial growth of gold on mica follows an island growth mode, temperature ramping between 150-300 °C tends to result in temperature dependent flattening of the surface. It is still questionable whether this flattening of the surface necessarily leads to better epitaxy between surface layers, and for that matter better AFM images. But it is clear, however, that temperature ramping is not harmful to gold(111) crystal growth.
The most important role that controlling the substrate temperature has in vapor deposition is that the temperature controls the amount of water present in the mica substrates. Water molecules provide nucleation sites for the growth of metal films.24 By increasing the temperature of the mica, there is less water present to provide nucleation sites. This in turn results in a reduction in the orientation of the initial nuclei, which gives rise to a reduction in the density of the nuclei forming the layers; and as a result, thicker films must be deposited to obtain extended epitaxy between metal layers.25 Just the opposite of this, reducing the substrate temperature allows for the growth of thinner films, as there is a higher density of water molecules to provide nucleation sites.26 The reason there is a limit to how low the substrate temperature may be kept and still allow epitaxial growth is that metal films grow with a liquid-like behavior.27 Secondary nucleation, in which growing metal islands provide the basis for filling in and growth of additional islands, is hampered by the presence of too much water, which impedes the epitaxy of the initial monolayers.

One final factor that controls the single crystalline quality of gold on mica is allowing the substrate to cool to room temperature before opening the system to air. While gold is not extremely reactive toward oxygen at room temperature, exposing the gold(1 1 1) to air, even at 40-50°C, resulted in much quicker oxide formation and degradation of the single crystalline surface.
III. Silver(111) Crystal Polishing

Polishing of the silver single crystal was a long, involved process which was never completely perfected. Polishing with 320 and 400 grit emery paper was done only once. The purpose of using such highly abrasive materials for the first step was merely to establish a flat, smooth base for further polishing. The following steps, involving many hours of polishing with 6 and 1 micron diamond paste on nylon cloth, achieved the goal of filling in and leveling out some of the deeper scratches caused by the emery paper.

The most notable change in smoothness of the crystal occurred after using a microcloth mounted on a polishing wheel, using successively 0.3 and 0.05 micron alumina. The polishing at this stage further filled in the scratches created by the more abrasive materials. The main purpose of polishing with alumina was only to flatten and fill the very superficial scratches on the silver surface.

During all of these mechanical polishing steps, a linear motion was used in moving the crystal across the polishing surface. By aligning all of the scratches on the crystal in the same direction, it was easier and quicker to smooth and fill in the surface while proceeding to smaller abrasive materials. When a random, circular polishing motion was used instead, it was much more difficult to get all scratches to a uniform size. Because it was more difficult to get the crystal to uniform smoothness at each step (when using a circular motion), the entire polishing process took longer and at the same time apparently gave no better results.
A couple of different chemical polishes were tried to further smooth the surface after all mechanical polishing steps were done. The first polishing procedure tried involved a concentrated HNO₃/CrO₃ polish, followed by a CrO₃/HCl polish. It was found, however, that this polish was too harsh. It seemed that the surface was oxidized by the polish, as the crystal was no longer shiny, but hazy and dull. AFM images were also unclear and inconsistent.

The other polish tried, which consisted of a NaCN/H₂O₂ polish and a NaCN wash, seemed to have relatively little effect on the clean alumina-polished surface. It did not dull the surface noticeably, suggesting that the polish was not too strong, but it also did not noticeably improve the quality of the AFM scans. One thing this polish was useful for, however, was cleaning the surface after UPD experiments. By repeating the chemical polishing procedure with this solution several times, the surface could in general be cleaned of any lead left over from the electrochemical experiments. Thus, by using the NaCN polishing solutions, it was generally not necessary to repeat the much more destructive alumina polishing procedures.
IV. AFM and Electrochemical Data

A. Results

For each of the UPD systems studied, perchlorate, acetate, and citrate, electrochemistry was first established in a teflon cell. Sharp UPD peaks were observed with each of the three electrolytes (Figures 4-6), using Hg/Hg2SO4 as a reference electrode. Similar CV’s were also seen in the same three systems when using a silver wire as a reference electrode. The UPD peaks in each of the three solutions were somewhat broader (ca. 2 times), when using silver as the reference electrode in the teflon cell. The peaks were also shifted from about 120 to 150 mV more positive, as should be expected.

All CV’s run in the AFM glass cell were referenced to a silver wire. A salt bridge was made from NaClO4, ten times the concentration of the electrolyte30, and used to connect the AFM glass cell to the Hg/Hg2SO4 reference electrode. Air bubbles and sealing problems, however, limited the effectiveness of this device.

For the each of two complete UPD/AFM experiments, data was collected at many different points along the deposition/stripping cycle. From the short range scans, fourier transforms were obtained for the regions of interest. From the fourier transforms, spacing between adjacent rows, and in some cases atoms, was determined. The data given below are representative examples of many potential regions explored throughout the UPD process. The scan rate for the each of the two separate experiments was 2 mV/sec., between times when the potential was held as indicated below. Normally,
potentials indicated were held from 10-25 minutes, depending on the stability of the AFM scans over time. Also note that for each of the potentials listed below, both long and short range scans were recorded.

<table>
<thead>
<tr>
<th>Potential (vs. Ag wire)</th>
<th>Scan Range (Å)</th>
<th>Spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.300</td>
<td>80</td>
<td>2.4-2.6</td>
</tr>
<tr>
<td>-0.462</td>
<td>530</td>
<td>2.5-2.7</td>
</tr>
<tr>
<td>-0.549</td>
<td>68</td>
<td>inconsistent</td>
</tr>
<tr>
<td>-0.669</td>
<td>260</td>
<td>2.7</td>
</tr>
<tr>
<td>-0.669</td>
<td>190</td>
<td>2.7</td>
</tr>
<tr>
<td>-0.744</td>
<td>250</td>
<td>3.3-3.5</td>
</tr>
<tr>
<td>-0.744</td>
<td>220</td>
<td>6-7</td>
</tr>
<tr>
<td>-0.895</td>
<td>90</td>
<td>3.3-3.5</td>
</tr>
<tr>
<td>-0.895</td>
<td>100</td>
<td>2.8-3.0</td>
</tr>
<tr>
<td>-0.895</td>
<td>100</td>
<td>2.8-3.0</td>
</tr>
<tr>
<td>0</td>
<td>160</td>
<td>5.7-6.0</td>
</tr>
<tr>
<td>-0.202</td>
<td>98</td>
<td>4.8-5.9</td>
</tr>
<tr>
<td>-0.202</td>
<td>98</td>
<td>3.4-4.6</td>
</tr>
<tr>
<td>-0.202</td>
<td>98</td>
<td>3.7-4.5, 5.2</td>
</tr>
<tr>
<td>-0.519</td>
<td>70</td>
<td>3.8-4.9</td>
</tr>
<tr>
<td>-0.640</td>
<td>100?</td>
<td>3.8, 7.3</td>
</tr>
<tr>
<td>-0.809</td>
<td>130</td>
<td>3.8-4.0</td>
</tr>
<tr>
<td>-0.809</td>
<td>130</td>
<td>2.9, 4.2-5.4</td>
</tr>
<tr>
<td>-0.809</td>
<td>290</td>
<td>3.6-3.7</td>
</tr>
</tbody>
</table>
The cyclic voltammograms for each of the two UPD/AFM experiments deviated from the more ideal CV's taken in the teflon cell. For the first experiment, the UPD peak occurred at -0.39 V vs. Ag wire, and the bulk peak at -0.723 V. For some reason, though, both the UPD and UPS (underpotential stripping) peaks were smaller than normal, and there was also a good deal of double layer charging (Figure 8). The CV from the second experiment showed similar effects, although in this case it was noted that the voltammetry became less well defined after cycling through the deposition/stripping cycle three or more times.

B. Discussion of UPD and Electrochemistry

There may be several explanations as to why the electrochemistry of the UPD process was not well defined in the glass cell. It may be that the silver crystal was not in ideal condition for running the UPD experiment, although this explanation cannot account for the fact that the electrochemistry was well defined and reproducible in the teflon cell. Interference from electrolyte anions must also be ruled out, as the same solutions were used in both the teflon and the AFM glass cells. It seems that the basis for the degradation of the CV's is most likely due to the cell geometry of the AFM glass cell (Figure 7).
Unlike the teflon cell, the AFM glass cell allows less contact between the electrolyte and the silver single crystal. It may be that depletion of the electrolyte is occurring more easily in the region of the crystal in the glass cell. As a result of this depletion, the cropping off of the UPD/UPS peaks could be explained, although there is no apparent diminishing of the bulk deposition and stripping peaks. If depletion of the anions were just occurring, this could explain a capacitance build up and the resultant double layer charging of the CV. This capacitance build up, in turn, may have some effect on the UPD, such as obstructing charge transfer which controls the initial kinetics of the deposition.\textsuperscript{16} This could subsequently explain the altered CV that was obtained. Although, normally, perchlorate acts as a good conductor and would therefore not tend to cause capacitance buildup.\textsuperscript{16}

The other factor occurring in the glass cell that does not occur in the teflon cell is that the working and reference electrodes are exposed to the working electrode only through narrow channels (Figure 7). This great reduction in the area of exposure of the reference and counter electrodes (in comparison to the working electrode) seems to cause conduction problems, as the electrolyte is not evenly exposed to all three electrodes. In the same AFM glass cell, when working with an acetate electrolyte similar conduction problems were found. They were remedied, however, by increasing the concentration of the backing electrolyte.\textsuperscript{31} The fact that the baseline of the CV's was slanted also tends to indicate that a cell geometry problem doth exist.

The concentration of the lead atoms, themselves, may have also had some effect on the nature of the observed UPD process. It is generally
accepted that when the concentration of lead cations is less than $10^{-2}$ M, the UPD process is diffusion controlled; but when higher concentrations of Pb$^{2+}$ are used, nucleation phenomena take control and anions effects become significant.\textsuperscript{16} In all three electrolytes studied, the concentration of lead was about $10^{-3}$ M. Therefore, anion effects should be expected to have little significance in affecting the UPD process, barring the possibility that they may limit transport and conduction, as noted above. After cycling through the UPD/UPS cycle several times, transport limitations of the solution may have caused the concentration of lead cations to be greater near the surface of the Ag(111). If this were the case, it is possible that the UPD process was incomplete because most of the adatoms were either on or very near the silver substrate, prohibiting deposition of a full monolayer.

Another factor which often affects the UPD process is the work function difference between the adatom and the substrate. In order for UPD to occur, the work function of the adatom minus the work function of the substrate ($\Delta\Phi$) must be (less) than zero.\textsuperscript{13} Although the work function difference between lead and silver obeys this, there still may be some other interaction, either among the lead atoms or between lead atoms and some contaminant within the cell which impedes UPD.

Another related element that may also affect the UPD process is whether or not the silver surface is single crystalline. If instead the surface is polycrystalline, consisting of Ag(111), (110), and (100), there is a great degree of variation among the work functions of the different silver faces. The work functions are respectively: 4.74, 4.52, and 4.64, while the work function of lead is 4.39.\textsuperscript{18} As the work function difference between the
adatom and substrate increases, the adatoms affinity for the surface becomes greater than its affinity for the bulk, thus favoring two dimensional surface growth over three dimensional bulk growth. The result of having a polycrystalline surface may be the simultaneous occurrence of three separate, though incomplete UPD processes. Each different crystal face would exhibit its own UPD fine structure, as well as showing different degrees of reversibility or hysteresis. The superimposition of these three UPD processes on the CV could very well lead to both broadening and distortion of the height of the UPD peak (as in Figure 9).

C. Discussion of AFM Spacing Data

Based on the study of the two dimensional fourier transform data of selected images, spacing assignments can be made in the images where row or atom corrugation is seen. When the silver crystal is scanned in air, surface structure is seen on a sub-micron scale (Figure 9). After adding the electrolyte, relatively little change is noted in the surface features of the crystal. Only when potential control is established, initially at 0 V vs. Ag wire, do the surface features change noticeably (Figure 10).

After exerting potential control on the system, it also becomes possible to observe atomic level corrugation. Between 0 and -0.59 V vs. Ag wire, any corrugation seen is expected to be silver(111) row spacing, as this range is prior to the UPD of lead. At certain points in this potential region no atomic spacing is observed. This may either be due to the fact the particular region being scanned is not smooth, or the surface may be contaminated by
foreign impurities, such as silver oxide. By establishing potential control, however, most oxide that may have formed from the crystal's exposure to air should be stripped off.

In the first UPD/AFM experiment, spacing in the pre-UPD region (0 to -0.549 V) was between 2.4-3.2 Å, with the majority of the spacing seen being about 2.6-2.7 Å. This data correlates reasonably well with the accepted silver face centered cubic row spacing of 2.888 Å.\textsuperscript{33}

In the second UPD/AFM experiment, pre-UPD data (0 to -0.519 V) have much less relation to the expected Ag-Ag spacing. None of the spacing observed is even reasonably close to 2.888 Å. At some of the potentials, spacing seen may be that of two rows of silver atoms instead of one. For example, at 0 V, spacing of 5.7-6.0 Å is seen, and at -0.202 V, spacing of 4.8-5.9 Å is seen. This spacing may coincide with an expected distance between two rows of silver atoms to be at least 5.8-6.0 Å. It is very difficult, though, to correlate any of the rest of the pre-UPD spacing data (with silver row spacing) from the second experimental trial.

In the UPD region, about -0.59 to -0.72 V, the spacing seen should be that of the initial lead monolayer. If the lead were cubic close-packed, commensurate with the silver surface, the spacing would be about 3.5 Å. The actual packing of the lead(111) monolayer, however, is cubic close packed incommensurate, with a spacing of 3.8-3.9 Å.\textsuperscript{34} In the first experiment, none of the spacing data taken in the UPD interlayer region, -0.669 V, corresponds to Pb-Pb spacing. Instead, the observed value of 2.7 Å still represents the silver(111) substrate spacing. In the second experiment, data taken at -0.640 V may correspond to Pb-Pb spacing.
Unfortunately, the spacing value in this region, 3.8 Å, is no different than spacing values taken at more anodic potentials as seen above.

Aside from the growth of the initial lead monolayer in the interlayer region (between UPD and bulk deposition), another process is occurring. Assuming the entire lead monolayer is deposited precisely at the UPD peak potential, the monolayer is two dimensionally compressed as the potential is made more cathodic, up to the point of bulk deposition. There is a direct linear relationship between the applied negative potential in this region and the compression of the monolayer, with the monolayer being compressed up to 2.8% relative to bulk lead just before onset of bulk deposition. This compression translates to a decrease in Pb-Pb spacing from 3.8 Å at -0.59 V to 3.7 Å at -0.725 V. There is no possibility of observing this compression, whatsoever, with the inconsistent data that was obtained. In order to see this voltage dependent compression, it would be necessary to study several points within the interlayer region.

Finally, in the bulk region (potentials of -0.725 V or less) only Pb-Pb incommensurate monolayer or bulk spacing should be seen. In the first experiment, at -0.744 V, the spacing values from 5.5-7 Å most likely represent two rows of silver atoms. At -0.895 V, the values of 2.8-3.0 Å correlate to Ag-Ag spacing. The value of 3.3-3.5 Å at this same potential may correlate to Pb-Pb spacing, although this value seems low for incommensurate packing. In the second experiment, several spacing values are seen at -0.809 and -0.908 V which probably correlate to Pb-Pb incommensurate packing. The larger spacings seen in this region, such as
4.2-5.4 Å at -0.809 V, and 6.0-7.1 Å at -0.908 V, are less easily identified. These values can just as easily equate to Ag-Ag spacing as they can to Pb-Pb. Judging from the long range scans of the silver(111) surface at different applied potentials (experiment 1), the surface structures can be seen to change throughout the deposition/stripping cycle. First, comparing 5000 Å scans of the surface, prior to the UPD region, at -0.462 and -0.549 V vs. Ag wire (Figures 11 and 12) there is almost no notable difference in the silver step structure. Even the image taken at -0.669 V (Figure 13), which is past the UPD region of lead, shows very little difference in observable surface morphology.

Only after cycling the potential out into the bulk deposition area at -0.895 V is there a significant difference in the surface features. The first scan, taken only a few minutes after reaching this potential (Figure 14), shows only limited changes from the scan in the UPD region. Eventually, after holding this bulk deposition potential for an additional twenty minutes there is a substantial change in the apparent features of the surface (Figure 15). By cycling the potential back to 0 V, it becomes apparent that some deposition process was in fact occurring, as the step features are much less well defined (Figure 16). By noting the height difference between the steps at -0.895 V and at 0 V, it appears that cycling back to 0 V did result in stripping of most lead that was deposited onto the surface.
D. Conclusions and Proposals for Future Work

The apparent problem with the first UPD experiment of lead on silver is that the growth process of the lead monolayer was incomplete. Although fairly conclusive evidence of face centered cubic silver-silver spacing was seen, there was no evidence for lead-lead packing in the UPD region. Even most of the spacings seen in the bulk region were probably due to silver.

The second UPD experiment also gave questionable results. Although most of the spacing data seen in the UPD and bulk regions of lead seem to indicate Pb-Pb incommensurate packing, the pre-UPD region spacings could just as well indicate lead spacing. Needless to say, the data from the first experiment are neither accurate enough, nor convincingly reproduced by the second experiment.

Several factors must be adhered to in order to provide reliable, reproducible data. It is first imperative to have a smooth, clean, single crystalline silver surface. It is further required to have reproducible electrochemistry. To overcome the problem caused by the geometry of the AFM glass cell, it seems necessary to increase the concentration of the backing electrolyte and thus eliminate transport or capacitance problems. Another solution could be to devise a microelectrode AFM cell that would potentially eliminate the problems caused by the isolation of the counter and reference electrodes. Based on the consistent silver-silver spacing data from the first experiment, it seems that the surface was honorable. The main problem seems to have been that either the sweep rate or the deposition was too fast.
or that the individual potentials were not held long enough for UPD to occur. If the growth process does occur very slowly, individual potentials should be held longer to allow time for equilibration of the electrochemistry.

In the first experiment, the UPD cycle was not run prior to recording AFM images. For this reason, it is known that no lead was electrochemically deposited onto the surface. In the second experiment, the UPD process was cycled through at least twice before collecting AFM data. There is a chance that, even though stripping of the lead was seen prior to beginning the AFM experiment, some lead remained deposited. Since the area of AFM study is so small (1.1 microns with the short range head), the phenomena being observed in one particular AFM experiment may not be representative of the more general surface processes.

After eliminating the problems associated with the silver surface and the geometry of the AFM glass cell, it will be interesting to collect UPD/AFM data on other electrolyte systems for comparison. With reliable electrochemistry, the effects of different anions on the kinetics and mechanisms of UPD could be studied. Nucleation and growth occur fastest in perchlorate, and slower in acetate and citrate, mostly because perchlorate shows lower capacitance. \(^\text{16}\) Perchlorate also does not form complexes with lead, whereas acetate and citrate do. \(^\text{15}\)

With AFM it may be possible to study the features of these complexes which may be adsorbed or desorbed onto the surface during the UPD process. It is possible that the mechanism and role these species play in UPD could be elucidated by more in depth surface studies. With carefully controlled experimental conditions, it should be relatively easy to study the
interaction of multiple species on the silver surface, whether those species are surface atoms, adatoms, or complexes. By gaining an atomic level understanding of the mechanism and kinetics of UPD, it will be possible to apply this knowledge to wide ranging problems involving the interaction between adatoms and metal surfaces in solution.
References

18. Discussion with Jerome Hubacek.
28. Personal discussion with Bryan Parker and Jerry Meyers.
29. Discussion with Bryan Parker and Dr. Andy Gellman.
31. Experiment done by Mr. C.C. Chen.
33. Chen's table of spacing data.
34. Personal discussion with Dr. Andy Gewirth.
Zone 1: Reactants area, normally the hotter end.

Zone 2: Products end, normally cooler end.

Zone 3: Far end of growth zone; ideally same temp as zone 2.

Outlet to turbo pump and sample loading. Glass wall is thinner in this area for torch sealing.
Figure 2 Bell Jar Evaporator

- Aluminum foil dome
- Thickness Monitor
- Mica pole holder
- Aluminum Shutter
- Glass Bell Jar
- Resistively heated tungsten boat
- Electronic Feedthroughs
- Vacuum outlet
Figure 3: Mica Sample Holder

- Tungsten filament heaters
- Grooved sample holders, lined with indium wire
- Insulated legs
- Copper plate
- Thermocouple
Figure 4: CV of Pb(111) in Perchlorate
Figure 5: CV of Pb(111) in Acetate
Figure 6: CV of Pb(111). Citrate

Bulk deposition -1.07 V

UPD -0.87 V
Figure 7: AFM Solution Cell (upside down)

Securing clip

Port outlets

Cantilever

Groove for o-ring

Ports for reference and counter electrodes.
Figure 8: CV of Pb(111) in Perchlorate (from first AFM experiment)

Bulk deposition -0.725 V

UPD -0.59 V

-0.3 V  -0.725 V