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PREPARATION AND CHARACTERIZATION OF LOW-DEFECT SURFACES

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MASTER

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Abstract

Silver crystal surfaces with low defect densities were prepared electrochemically from aqueous solutions using capillary-growth techniques. These surfaces had low rates for the nucleation of new silver layers. The impedance of these inert silver/aqueous silver nitrate interfaces was used to determine silver adatom concentration and water dipole reorientation energetics. At room temperature, the normalized silver adatom surface coverage is low, $\theta = 2.7 \times 10^{-3}$, and the reorientation enthalpy (ΔH) of water dipoles is $-24.5 \text{ kJ mol}^{-1}$. Growth of silver crystals that contained redox-inactive, nucleation enhancing defects resulted in unusual temporally-deterministic monolayer growth events. Study of the waiting time between these growth events allows determination of surface diffusion coefficients for silver adatoms. We calculate $D_s = (1.2 \pm 0.3) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at $T = 20^\circ\text{C}$, and $D_s = (2.5 \pm 0.9) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at $T = 50^\circ\text{C}$.

Computational techniques were applied to the determination of time-dependent microscopic growth rates and to the simulation of diffusive mass transport at low concentrations in a chemical potential gradient. Monolayer growth resulting from expansion of a circular growth front into an elliptical boundary was analyzed and algorithms were developed for converting experimental observables into the initial location of the nucleation site. For a boundary with minor axis length

77 μm and an eccentricity of 0.65, the methods determine the nucleation site to within a mean deviation of 540 nm from the actual site. The mass transport simulations were performed on a finite one-dimensional lattice and the results were extended to adatom transport across macroscopic surfaces.

Techniques and instrumentation for scanning tunneling microscopy and spectroscopy were developed. Simultaneously acquired topography and differential conductance data were visualized by texture-mapping color-coded conductance data onto a three-dimensional representation of the topography. This visualization technique allows correlation of electronically unique surface features with local structure. For example, terrace regions on polycrystalline platinum surfaces demonstrated work function differences on the order of 1 eV. Steps on highly oriented pyrolytic graphite (HOPG) were observed to have significantly lower work function than surrounding terrace regions by 1 ± 0.5 eV. Faulted and unfaulted surface layers of HOPG were found to exhibit different differential conductance, consistent with small work function variations between the surface structures.

DEDICATION

This thesis is dedicated to the memory of my mother,

Helen Louise Robinson

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PREFACE

The focus of this work is the study of defects at surfaces and interfaces. Here, defects are defined as deviations from ideal surface structure in the form of point and larger structural defects, steps and one-dimensional defects at steps, and physical adsorbates or chemical inhomogeneities which modify surface behavior. Defects are important because they are often more chemically reactive than other (more ideal) regions of surfaces. An understanding of the nature and reactivity of defects is essential to the understanding of "realistic" surfaces and interfaces that contain a mixture of ideal and defective regions. The approach here is to apply surface-sensitive detection techniques to study surfaces and interfaces with low numbers of defects in order to discover chemical, physical, or electronic information about those defects.

In general, our tool for probing surfaces and interfaces is the electron. Here, electrons are not employed as surface sensitive scattering tools, as they are commonly used in surface science. Rather, high-precision electron counting is applied as a surface and interfacial probe. Present technology allows detection of electrons in "blocks" for sustained periods or as single electrons up to a limited, but considerable, charge. We apply the former technology and use special circumstances to attain high surface-sensitivity. This work presents two types of experiments in which electrons are counted by the currents that they generate.

The first type of experiment uses the transfer of electrons to and from localized electronic states to measure the stages of a surface chemical reaction. Low-defect crystals of silver are prepared by growing silver crystals down a capillary tube. These low-defect surfaces are characterized by an interfacially sensitive technique, impedance spectroscopy. The surfaces of these crystals are then used as substrates for the study of monolayer nucleation and growth. Study of the reaction rate during discrete monolayer growth events not only reveals the kinetics of the growth reaction, but also information about defect site location and reactivity. These studies have also allowed what we believe to be the first direct determination of the diffusion coefficient of a metal atom at a solid/liquid interface.

The second type of experiment uses the elastic tunneling of electrons between delocalized electronic states to measure the structure and properties of conducting materials. These experiments fall into the categories of scanning tunneling microscopy and spectroscopy (STM/S), with which the reader may be familiar. We have constructed a STM/S instrument that is optimized for acquiring simultaneous images of topography and conductance. Due the ambiguity in the interpretation of topographic data alone, we have found that the application of complementary techniques is required to obtain chemical, physical, and electronic information regarding defects at surfaces or interfaces.

This thesis addresses these experiments in the following manner. Chapter one presents the background, experimental protocol, and results of the silver crystal growth experiments. Chapter two focuses on computational issues that developed from the work in chapter one;

namely, simulations of monolayer growth and surface diffusion under low surface concentrations. Chapter three describes our scanning tunneling microscope and some experiments on "realistic" surfaces in air. A summary of all the work and some additional comments are provided in the closing chapter, chapter four.

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CHAPTER 1

PREPARATION AND CHARACTERIZATION OF LOW DEFECT SILVER CRYSTAL SURFACES

Introduction:

Experimental work in the field of surface science has greatly added to the fundamental understanding of many practical chemical systems^{1,2}. Visualizing physical surfaces as more than mere planar boundaries between solids and other phases has been crucial to these advances. In the plane of the surface, the presence of deviations from ideal packing (defects) often leads to dramatically different chemical and physical behavior in comparison to the ideal surface. It is very important, then, to characterize the number densities, structure and reactivity of surface defects. Application of results from vacuum surface science to the understanding of real interfacial systems can often be hindered by the complexity of typical surfaces and interfaces. Details which must be considered when thinking about or describing such a system are numerous, making sample preparation and the choice of system of study critical. What is needed are experiments which can probe more complex systems yet still retain enough simplicity to provide fundamental understanding.

Defects at surfaces can dominate catalytic chemical behavior in many circumstances. One class of examples are found in the area of nucleation and growth³⁻⁸. The rate of formation of a new phase from a supersaturated solution can be dramatically enhanced by macroscopic or microscopic defects. To model growth and deposition of thin films, it

is important to understand the formation and reactivity of defect sites that promote growth.

Growth-promoting sites actually can take many physical forms such as point defects, atomic steps, kinks in steps, and general stacking faults. Information regarding these sites can come from different types of experiments. At present, work in many areas has begun to address the roles of defect sites in broad terms⁵⁻⁸. In most systems, microscopic details of defect structure and reactivity are still unknown. In modeling a real system, knowledge of the number density of these sites and their activity are critical clues to the time evolution of the system. Another key piece of information to obtain is a physical map of the locations of these sites. Such a map could be a useful tool in the structural characterization of defect sites and investigation of structure-reactivity relationships. Our experimental work has been focused on the study of surfaces with almost perfect structure and the characterization of the remaining defects in these ideal systems.

In the growth of homogeneous (like-upon-like) systems, meaningful information can be obtained about defect sites and their reactivity. These interfaces, either solid/gas or solid/liquid, have been the subject of research for a considerable period⁴. The most detailed experimental work studying microscopic growth issues has been done rather recently^{9,10}, compared to the historical interest in the field¹¹. The process of growth can be summed up as the condensation of small growth subunits from a supersaturated phase into the solid phase. Supersaturation may be created in several ways. In the gas phase, a vapor or partial pressure of the atoms may be exposed to the substrate,

resulting in bulk growth. In liquids, an electrochemical potential can provide a driving force for net deposition. The process of initiating bulk growth is the nucleation of a new solid phase on the substrate. Usually, certain types of defect sites on the surface activate growth via reducing the critical cluster size required for nucleating a new phase³. In this case, even modest supersaturations produce growth which proceeds in a regular, deterministic manner. Occasionally, the defects on the surface can act as catalysts for growth through much larger critical clusters. Here, the correct supersaturation conditions produce net growth by a series of many microscopic events. It is through the study of these microscopic events that defect reactivity and system growth dynamics can be determined.

Historically, microscopic growth models have centered around the dimensionality of the net growth¹². One category of growth is characterized by the three dimensional growth of isolated islands on top of the substrate. This type of growth is known as Volmer-Weber growth. Another growth mechanism is the two dimensional expansion of atomic or thin flat layers. In this case, the new phase makes a homogeneous 2-D layer over the old phase. Note that this growth model does not stipulate that the growth in a particular layer must be completed before the growth in a new layer begins; it simply excludes the presence of isolated islands. This is the nature of Frank-van der Merwe type growth. Experimental evidence also exists to support a mix of these two categories. In this mix, the Stranski-Krastanov mode, a few layers (2-D) are uniformly deposited over the substrate before the growth of the 3-D

islands commences. One recently published example with good references can be found in the work by Taylor et al¹³.

Selection between growth mechanism is often determined by the chemical system involved^{12,13}. The surface energy differences between phases and the degree of supersaturation play key roles in determining the dominant growth mechanism. One can generally describe the competition of various growth models as a balance of lateral and vertical growth rates. In the growth of many homogeneous systems, surface defect type and amount of driving force for growth combine to determine the growth mechanism. It is possible to force systems into one mechanism or another via external means which affect these variables. For heterogeneous systems, the same can apply. However, the surface energy differences between the two solid phases (substrate and new growth) control the early stages, producing in many cases, layer-by-layer growth followed by island formation.

One very important subset of the layer-by-layer growth model is the self-propagation of screw dislocations emerging at the surface of a crystal. A seminal work on this mechanism was published by Burton, Cabrera and Frank in 1951³. Screw dislocation defects are members of the class of defects which can promote growth via very small critical cluster size. The atomic step line extending from the emergence point of a screw dislocation provides a catalytically active site for growth. Growth may proceed at screw dislocations at significantly lower driving force or supersaturation than on planar defect free crystal surfaces. In general, auto-catalytic growth of steps proceeds at lower supersaturations than the nucleation of entire new phases.

Our system of study is the growth by electrochemical reduction of silver ions to form silver single crystal surfaces,

This is a simple and useful system for several reasons. The electrochemical reduction is quite reversible under typical conditions and is well behaved electrochemically. The very positive reduction potential of Ag^{+} also tends to prevent co-deposition of many metal contaminants. Finally, large amounts of work on the silver reduction system has been conducted because it is perceived as a model system. General study of silver polycrystalline surfaces has been done by several other groups^{9,15-20}, indicating interest in the system and its relevance. Work by the Bulgarian Academy of Sciences towards low surface defect preparation of silver crystals has been conducted for several years^{10,21-29}.

Research by Budevski and coworkers on silver single crystal growth has substantiated the claim that ultra-low defect single crystals may be prepared by capillary growth techniques^{10,21,26}. Silver single crystals (usually Miller index {100} planes) were placed against the mouth of 200 micron diameter capillary tubes. While electrochemically depositing silver on the surface, growth down the capillary was observed. In some cases, the authors observed that the growth rate in some capillary tubes slowed dramatically. By studying the instantaneous rate of growth (the reduction current) the growth process was observed as a series of discrete events. Each growth event consisted of nucleation and layer

growth processes. The layer heights were found to be monatomic by counting the number of electrons in each growth step. Our interests in this system center on reproducing these results and studying the microscopic growth of these thin metal films in detail.

Information which can be obtained from experimental studies of these silver surfaces falls into the following areas; adsorption, energetics and dynamics of adsorbed species, growth rates of thin films, and details of number density and activity of surface defects that affect growth. We have used a.c. impedance³⁰ techniques to measure equilibrium values for silver adatom populations and organization energetics of the interfacial double layer. Analysis of nucleation and growth events has revealed layer growth rates, shape of expanding growth islands and defect site locations. Finally, by studying sets of growth events, we have observed signatures of surface diffusion and quantified the results at two temperatures.

Experimental:

Three parts comprise this experimental section; electronics design, capillary cell design, and experimental techniques. Since the electronics used in these experiments were made in-house and reflect an original application of low noise analog circuit design and digital interfacing, a careful description will be provided. The experimental cells used here are of common design³¹; minor modifications are made to accommodate the capillary experiments. Experimental techniques discussed here cover both the preparation of low defect surfaces and their characterization *in situ*. Characterization techniques in this

experimental context include a.c. impedance studies, equilibrium measurements of the nucleation process, and time dependent monitoring of the microscopic growth process.

In order to operate over widely varying time scales, considerable effort must be applied toward minimizing noise in the electronic circuitry. Fundamentally, these electrochemical experiments are based on the control and measurement of electrical potentials and responses to the potentials in the form of current. Noise in these signals will degrade the quality of the experiments and the results, so this is a very important issue in the design of the experimental apparatus. Two of the best defenses against laboratory electrical noise are careful shielding and good circuit design^{32,33}. System noise can also be reduced by limiting the response window of interest, both in signal size and bandwidth of the signals. Our research in the design of these types of experiments has required the application of all of these tools and some linear averaging to reduce noise. Using the temporal needs of a particular characterization method to determine the exact combination of the above techniques has been crucial in the battle between signal and noise. The system design required considerable flexibility, so the designs presented here not only represent a good solution to the problem at hand but also show ideas ready for generalization.

The basic problems which the experimental apparatus must solve are multiple and coupled. To control the electrochemical cell, a potentiostatic circuit with low noise is required. These experiments with silver nucleation and growth require a range of applied d.c. potentials of ± 100 mV with a precision of 10 μ V. Measuring the rate of

growth is done by converting the reduction current into a voltage. For capillary tubes on the order of 100 microns in diameter, the total charge passed in the deposition of a monolayer metal film is about 10 nC. Over the growth period of a second, this is an average of 10 nA. Our apparatus needed to handle currents up to 200 nA with a precision of 0.05 nA. Previous experiments^{10,21,26,27,29} of this type have used chart-recorder type technology to record long time series of growth events. In our work, we have interfaced a computer to the apparatus to automate cell control and data analysis. While this addition provided a significant advance in the accessible data set size and enhanced data analysis capabilities, removal of the electrical noise caused by the computer required extra effort due to our small signal sizes.

Computers, fortunately, are well suited to handling large volumes of data. Our expectations based on the previous work were that time series data should be acquired at rates of 1,000 to 10,000 times per second, for extended time periods. With the help of an AT&T 6300 plus (AT compatible) we were able to record up to 240,000 points at a time. The conversion from analog to digital signals was accomplished by a Labmaster (Scientific Solutions) experiment interface board. Signals to the analog-to-digital conversion system were locally buffered, preventing the computer inputs from providing an easy path for noise introduction. Our maximum rate of conversion, retrieval and storage of data points was at 10 kHz. This gave 24 seconds of run time for our best temporal resolution. Although adequate for recording a few growth events with very fine resolution, recording time series with many growth events required the use of a slower sampling rate. It is interesting to

note that a personal computer of similar price today would be able to attain higher sampling rates by at least a factor of 4 and total data point storage per experiment sixteen times larger. Our computer generated the experiment control signals via the Labmaster board. The digital-to-analog conversion was done with 12 bits of precision (1 part in 4096), however the electrical noise of the computer contaminated the lowest 2-3 bits in wideband output situations. This was solved by increasing the rise time of the output signal to 10 ms via a passive low-pass filter. An additional step to reduce the impact of computer generated noise included the design of an internal adjustable voltage source, allowing the computer-based potential control to be disconnected during some experiments.

The small electrical circuits for the apparatus were constructed on industry standard double-sided copper-clad polycarbonate boards. All of the electronic circuits were placed on boards by signal type and function. Input potentials and local control signals were generated on the top-level board. This board had the most direct contact with the "outside" world. Immediately below, a board with two buffering circuits amplified small signals from the precision experiment control board to high levels. The experiment control board housed the potential control and current monitor circuits. In the initial experimental configuration, the experimental cell was also housed on this circuit board. The power supplies for these circuits were two 6 amp-hour motorcycle batteries. These chemical voltage sources provided stable and very low noise power for several days to the electronics.

The electronics, experiments and power supplies were enclosed within a 1 cubic foot Faraday cage. The Faraday cage was constructed out of copper-clad 1/4" mild steel plate and had holes drilled into the back with one inch spacing for input and output of electrical signals and thermal control fluid. This cage determined the design definition of "inside" and "outside" world signals. To prevent contamination of "inside" signals through direct and capacitive coupling, noise reduction techniques and careful shielding were applied on all signals from the "outside" world heading in. The boards were mounted within the Faraday cage on a series of interconnected 15 pin connectors. The top-level card was connected to the "outside" world through BNC bulkhead mounts in the back of the Faraday cage. The buffer stage was connected to the top level card and the small signal stage, and physically resided between those boards, just below the top-level card. In the following paragraphs I will present schematics and explanations of the building blocks for these experiments. The pin numbering is included here for completeness, but detailed descriptions of the individual integrated circuits are omitted since they are well discussed elsewhere³³.

Illustration 1 is a schematic of the top level board. The task that this board was designed to accomplish is the control of potentials applied to the experiment. One circuit produces a square wave signal centered about zero volts. It uses a 555 timer to generate a 50 Hz, 360 mV peak-to-peak signal when the relay enabling its output is closed. The timer is powered by the relay control signal, turning the oscillator on only when its signal is allowed to pass to the experiment. The output stage divider with 1.1 k Ω to ground is also the input for the

computer based potential signal. The series resistance of that signal is 110 k Ω producing a 100 times division of the input signal. The combination d.c. signal from the computer and the square wave signal are propagated to the experiment control board together. The other component of this board is an adjustable negative voltage regulator. This produces a signal of 2 to 20 mV at the output with correct sign to drive the reduction of silver ions onto the working crystal surface. A local potential source of this type provides very low noise and low drift operation by eliminating the need for external potential input. This signal is not combined with the other potential control signals on this board because an active component would be required to correctly add the small level d.c. signals. Part of the control small signal electronics conducts the summation.

Illustration 2 is a schematic of the two functional blocks on the buffer board. These are both simple operation amplifier circuits. The industry standard 741 amplifier is configured as an offset nulled non-inverting 40 dB amplifier. This circuit buffered the output from the potential monitor on pin 6. With nulling of this stage, measurement of the millivolt signals of the potentiostat could be accomplished with an accuracy of 5 μ V. The adjustable feedback loop amplifier was used as both adjustable bandwidth and adjustable gain amplifiers during these experiments. As drawn, the relay position determines the effective bandwidth of the amplifier, keeping the amplifier gain constant. This amplifier acted as the buffer for the output of the current to voltage converter on the small signal stage. The basic purpose of this stage is to condition the outgoing signal toward the appropriate response

bandwidth and noise level of the characterization technique. The relay position which selects the path containing the 2000 pF parallel capacitor is used for recording time-based, narrow bandwidth, low d.c. noise current data. The other position enabled faster response of this stage and served as the setting for the a.c. impedance experiment output source.

Illustrations 3 and 4 depict the circuits which required the most design effort. Illustration 3 is the three electrode potentiostat circuit used in most of the work reported here. The second complete board design represents the optimal circuit design for this type of experiment and was developed in steps during the experimental work. Both represent very simple, low noise solutions to experiments which need to make precision current measurements in electrochemical systems. The three electrode circuit supports the typical counter, reference and working electrodes and works well with currents on the order of nA, controlling potentials with microvolt precision. The quality of the input signals and reference electrode type will usually determine the precision, rather than the circuit itself. This circuit maintains stability by using the cell as part of the feedback for the potential control amplifier. This summing amplifier takes inputs of d.c. and a.c. voltage and generates an output within the experimental cell that produces a match to these inputs at the location of the reference electrode. The control amplifier in this design is able to source 10 mA and 10 V to accomplish this task. The amplifier connected to the reference electrode acts as a buffer to the signal returned from the experimental cell. The output of this buffer goes to pin 6 where it is

amplified to "outside" world levels. The amplifier attached to the working electrode converts the current running through the cell into a voltage. The transimpedance gain of this block is 2×10^7 V/A while the small signal response bandwidth is around 2 kHz. However, this response width strongly depends on the total resistance in the experimental cell. When the cell configuration was modified to reduce the capillary length and its resistance, this circuit design proved to be too slow in response to allow frequency domain experiments. Despite its slow performance, the analog devices AD549 low input current amplifier delivered outstanding time domain response and exceeded our needs for a nA current measurement device by a fair margin.

The original three electrode potentiostat circuit evolved into the two electrode apparatus in illustration 4. Our symmetric and chemically simple system made the use of a reference electrode redundant when little or no current was being passed through the cell. By using local feedback to the summing control amplifier, the noise above 1 kHz to the cell was dropped by about 5 times. The amplifier used in the current measurement step is a very fast, low input current uncompensated op-amp. This resulted in significantly widening the bandwidth of the current measurement. The high impedance lead from the experiment had to be further shielded to prevent this bandwidth widening from significantly degrading the final output quality. The additional shielding was accomplished by bootstrapping a guard around the signal lead to the potential of the lead. This is a common trick used to decrease the apparent impedance of a line and reduce its antenna-like behavior. This converted the original coaxial wire, (inner signal with an outer ground)

R_{cell}	0 Ω		50 k Ω		100 k Ω	
f / Hz	Gain/dB	phase	Gain/dB	phase	Gain/dB	phase
10	0.0	1.2	0.0	1.0	0.0	0.8
100	-0.027	-2.0	-0.033	-2.3	-0.0059	-2.3
1k	+0.011	-2.6	-0.049	-4.5	-0.071	-4.6
5k	+0.76	-9.6	-0.58	-11.6	-0.71	-11.7
10k	+0.53	-31	-1.3	-16.6	-1.6	-15.5
20k	-3.3	-50	-2.4	-22.6	-2.5	-19
50k	-8.9	-53	-4.6	-31.9	-4.1	-27.5
100k	-12	-58	-6.9	-44.7	-6.0	-40.8

Table 1. Gain and phase response of optimized experiment control circuit. The gain is reported in dB shift from low frequency values. Phase is reported in absolute shift in degrees from the input signal.

to a triaxial wire of signal, guard, and then ground. The response bandwidth of this design was orders of magnitude better with only a factor of 3 increase in d.c. noise for very low cell resistances. A sample of the response curves vs. frequency for a model experiment characterized by a simple resistor in parallel with the input 10 k Ω resistance is shown in Table 1. The 10 k Ω resistor is used to set a bound on the instrument response which can be calibrated. The flat, 6 to 12 dB loss over 100 kHz, response is nearly the best possible for circuits which set out to measure currents on the order of nA and smaller. However, the application of this design is limited to systems where two electrodes are sufficient and the presence of an uncompensated resistance of 10 k Ω is acceptable.

To close the description of the electronic apparatus, an outline of the computer operations and software follows. As mentioned earlier, the computer controlled the experiments and data acquisition. Computer control came in the form of both analog signals to the cell and drive signals for the relays on the circuit boards. The bulk of the data acquisition here was retrieval of digital data from an analog to digital converter. This data was saved in the computer's memory. Once the memory capacity was filled the data were written to files on a hard disk. The hardware link between the computer and experiment was established with the Labmaster board. This board was mounted within the computer and provided the digital signals, analog outputs and inputs needed. The digital signals were amplified in capacity by transistors to drive the relays. One of the board's analog outputs was filtered and sent to control cell potential. The analog inputs converted both current and applied potential signals into digital values with 12-bit precision. The software to operate the hardware link was written and compiled in the Microsoft QuickBasic 4.0 environment. Source code for the experiment operation, data acquisition and data viewing is included in Appendix A. A program designed to control and monitor the early stages of growth of the crystal down the capillary was developed, GROWSAMP.BAS. A single integrated program WRKSPCE.BAS ran all experiments and controlled steady state cell conditions via a menu interface. The size of the control program was kept small to allow for maximum storage within the computer memory space. The control program ran potential step and constant potential growth experiments directly. It sent control signals and ran experiments with a Princeton Applied

Research model 5208 lock-in amplifier through a GPIB interface card (National Instruments PC-IIA). Another program, FILEPLOT.BAS was employed to read and scan through saved time-series data. This program generated output on a Hewlett Packard 7475A plotter via the GPIB interface.

The experimental cell used in these experiments was a threaded teflon cap with a glass bottom, providing a total volume of 10 mL (see illustration 5). The teflon cap was machined to accommodate three 1/16" diameter tube swagelock fittings. Two holes were on the side of the cap; these served as inlet ports for the counter and reference electrodes. The last hole was in the center of the cap, allowing a straight path through the cap for the working electrode. The base of the cap had a 6 mm diameter hole which provided a mounting site for the capillary tubes. The glass and teflon parts were easy to clean and provided inert containers for the concentrated silver nitrate solutions used in the experiments. During the course of experiments, reference electrode configuration and capillary type were varied.

The counter and reference electrodes were constructed from 0.25 mm diameter silver wire (Alfa 99.9%). The counter electrode was a bare wire inserted through the teflon cap after cell filling. The reference electrode evolved during the course of the experiments. Originally, all but the tips of the silver reference electrodes were sealed in glass. A bend was placed in the glass to position the end of the electrode at the capillary mouth. Most of the glass seals leaked, however, and the reference electrode in later experiments was another bare wire bent towards the capillary mouth. In fact, potential control through the

reference was at times unreliable; this issue is analyzed in the discussion.

The working electrodes were designed to provide an electrochemically inert surface that would act as a substrate for the growth of silver seed crystals. One good material for this is platinum. Platinum wires of small diameter (less than .20 mm) are easy to seal in ordinary or hard glass. Our working electrodes were constructed of short lengths of .125 mm diameter Pt wire sealed in glass tubes. One end of the wire was completely embedded in glass while the other end was attached to a larger diameter silver wire. The silver wire extended out the unsealed end of the glass tube, providing contact to the Pt electrode. The embedded end of the Pt wire was exposed by a series of polishing steps. The coarse step was done with 400 to 600 grit sandpaper until a regular disk of platinum was exposed and surrounded by glass. The remaining steps were polishing this surface with a series of decreasing size alumina particles. The particle used ranged in size from 1.0 μm down to 0.3 μm and they were supported on ordinary filter paper. Methanol was used to prevent the particles from sticking together. The polishing process was checked for completeness between steps with a 100x optical microscope. The final surfaces appeared mostly flat, with some detectable scratches. Overall, the surfaces had a fair mirror finish after 20 minutes of polishing. A well polished and cleaned Pt electrode resisted nucleation of silver crystals to overpotentials of 30 mV with respect to a silver polycrystalline wire. These surfaces were sufficiently inert to allow the formation of only a single crystallite, and not multiple crystals during seed growth.

Two capillary configurations were used. Initially, capillary tubing from Wilmad Glass was employed. These tubes had a total length of 0.5", an outer diameter of 6 mm, and a bore diameter of 76.2 μm . When filled with electrolyte, the capillary resistance to current flow of these tubes was quite large because of their length. To obtain capillary tubes with lower resistance, short capillary tubes were made by spinning the end of 6 mm Pyrex glass tubing in a torch flame. In the flame the end of the tube melted and collapsed, producing capillaries of length 1-2 mm with bores comparable to the commercial capillary tubes. The capillary tube had an hourglass shape after formation (see illustration 6). Black wax was pulled into the capillary to prevent damage to the tube during abrading and polishing. The capillary was abraded until the region with the narrow bore was exposed at the end. The end of the capillary was then polished to a smooth finish. Finally, the wax was removed from the capillary by combustion in a flame. The capillary tubes of both types were cleaned first in methanol saturated with potassium hydroxide (KOH/MeOH) and then in *aqua regia*. After this the capillaries were rinsed with ultrapure water and exposed to dichlorodimethylsilane ($\text{Cl}_2\text{Me}_2\text{Si}$) by placing them in a 150 mL beaker with one drop of the solution and covering with parafilm. After 6 to 24 hours the capillaries were hydrophobic, as verified by failure of capillary action with water.

Temperature control of the experiments was obtained by exposing the cell to a solution circulated in a thermostat bath (Neslab model RTE-5DD). The solution used in the bath was a 1:1 Prestone anti-freeze to water mixture. This bath solution was circulated around the cell two

ways in these experiments. Illustration 7 shows the cooling/heating schemes. The plexiglass jacket probably provided better temperature control since there was direct contact between the bath solution and the experimental cell. The copper coil worked by proximity thermal control alone and required additional insulation (cotton gauze was wrapped around the coil). However, use of the copper coil and the short capillaries allowed optical observation of the growing silver crystals throughout a given experiment. The objective of a 100x microscope was placed in one open end of the copper coil. This microscope could focus over the entire length of a properly positioned and polished short capillary. This configuration significantly enhanced observation and quality control while meeting all of the other experimental design parameters.

Initial seeds for the experiments at the Bulgarian Academy were large silver single crystals. To place the crystals close to the mouths of the capillary tubes, however, these high quality crystals were sanded to fit. This rough treatment can damage the crystal significantly due to silver's low energy of activation for slip plane propagation³⁴. We developed techniques to grow small low defect seed crystals ex and in situ on platinum and other small electrodes. For silver, these high quality single crystals can be grown to dimensions on the order of a few hundred micrometers across. On Pt disk electrodes sealed in glass, the seeds were grown from an aqueous solution of 3-5 M AgNO₃ containing 0.1 mM HClO₄. A single microcrystalline seed was formed on the Pt electrode by the application of a -30 mV potential (with respect to a polycrystalline silver wire) to the clean electrode until current begins

to flow. Typically, the background current is less than one nA, and once the silver crystal begins to grow, the current rises above 50 nA. Higher initial potentials tended to produce multiple separate crystals. Once the current started flowing, good crystal geometries were formed for growth potentials between -15 and -20 mV. Total charge passed per seed crystal was between 10 and 20 mC. The seed crystal morphology and quality were checked with a 100x optical microscope. Optically, the seed crystals appeared to be bounded by flat facets with sharp boundaries between facets. Six sided facets usually dominated these microcrystals although some rectangular to square facets were present. These crystals were also grown on a small diameter carbon fiber but the adhesion to the Pt surface was much better. For seeds grown on platinum, it was possible to lift the whole glass electrode by placing the tip of a razor blade against the seed crystal. This turned out to be a convenient check of the adhesion of the seeds, although it was usually used to check preparation techniques rather than test individual seeds.

The cell equipment was cleaned in a saturated potassium hydroxide in methanol solution followed by *aqua regia*. Parts were rinsed in ultra-pure water (Millipore Milli-Q system) and the teflon cap was kept in H₂O overnight to leach out chloride ions adsorbed while in the *aqua regia*. The experimental cell was filled with a solution of concentrated silver nitrate by a syringe. All of the experiments used 5.0 M AgNO₃ prepared from pure crystals (Fisher A.C.S.) and ultrapure water. Near the end of the experimental work, varying amounts of perchloric acid were added to study low pH versus nominal pH. In addition to varying

pH, the oxygen content of some of the solutions was reduced by bubbling with N_2 for 10 to 20 minutes. Before filling, the cell was assembled by screwing on the teflon cap with capillary tube and reference electrode installed. A teflon syringe tube was passed through the counter electrode entry hole to fill the cell. To get the solution to enter the hydrophobic capillaries, a small amount of vacuum was applied to the top hole in the teflon cap, sucking the solution up the capillary. After the cell was filled, the counter electrode and the working electrode with seed crystal were installed. Care had to be exercised to prevent bumping the working electrode and shearing the seed off the end of the electrode. For the long capillary tubes, the seed and capillary could not be seen after assembly because the end of the capillary was within the teflon cap. With the shorter tubes, quality control was much better.

Once the seed was placed at or near the capillary mouth, the cell was mounted within the Faraday cage and connected to the control electronics. A d.c. potential was applied to produce net growth while a larger amplitude square waveform was applied at a frequency of 50 Hz. Some experiments assessed the effects of potential applied and the frequency and magnitude of the oscillating potential. The effects of cell temperature on growth morphology in the capillary were studied in the range of 0 to 60°C. Typical conditions used in the initial growth segment were applied potential of -25 mV, oscillator amplitude 200 mV peak-to-peak and thermostat bath temperature 40°C. The crystal was grown down the capillary until signs of reduced surface defect density appeared in the current response. In the long capillary tubes, this

occurred over a few millimeters from the capillary mouth. In the shorter capillary tubes, the crystal often grew through the full length of capillary and out into the main solution volume. The ideal capillary length is probably on the order of 2-5 mm, between the lengths that we had at our disposal.

The current response to the applied square wave was one guide used to determine the reactivity and defect density on the growing crystal. The response of a simple resistive cell to the input square wave would be a square response plus a current from double layer charging at the interface. For a surface with a large number of active sites or a few exceptionally active sites, this type of response was observed. When the number or activity of the growth promoting sites decreased, the response to the applied square wave changed. Illustration 8 shows a typical comparison of these two situations as viewed by an oscilloscope. The change in response is due to a change in the growth mechanism. When nucleation of new layers or nucleation of pits at the interface become an important part of the net reaction, the temporal response takes on a slower, delayed form.

Another guide that we used to study defect density and reactivity was descriptive statistics regarding the instantaneous growth rate. During the growth of the crystal within the capillary, the computer changed the applied potential from -25 mV to -6 mV and turned the oscillator off at regular intervals. After a relaxation period of four minutes, the computer acquired a large number (ca. 5000) of readings of the current over the course of a minute. The program then printed out the applied potential, the mean current, the standard deviation and some

other descriptive statistics. After printing out the data, the growth experiment was resumed at the previous conditions. The computer automated long experiments through this growth data sampling program. Usually, the data sets were acquired every 30 minutes with total run time of the experiment in the long capillaries of a few days to one week. By looking at the mean current, a quick estimate of the reactivity of the surface could be obtained. However, this one value did not describe the time-based behavior. For example, one could not tell the difference between slow growth caused by a broken contact vs. slow growth due to an inert surface. During periods of slow growth on low defect surfaces, a major component of the growth current was due to fluctuations caused by microscopic nucleation and growth events. The normalized deviation and skewness of the data were used to measure the magnitude of these fluctuations and their deviations about the mean. Armed with these tools and techniques, we went in search of the "fake-atom smooth"²¹ surface.

First observations of non-typical interfaces appeared in the form of non-reactive or inert surfaces. This behavior was first recorded and studied by slow potential sweep experiments. A computer program was written to look for signs of the onset of growth activity of these interfaces. The program started at a small reductive potential, -1 to -3 mV, and incremented the potential in small steps with a few seconds between each step. This produced a steady state potential sweep experiment. From these experiments it was possible to measure the overpotential required to trigger growth. These data also allowed an estimate of the rate of supercritical cluster formation at the onset

potential. The inert interfaces were subjected to large amplitude potential pulses of short temporal duration to "jump-start" the growth process.

Inert interfaces were also characterized by impedance spectroscopy techniques. An oscillating perturbation of 33 $\mu\text{V}(\text{rms})$ was applied to the counter electrode in addition to the d.c. overpotential. The current response to this signal was detected by a Princeton Applied Research two-channel lock-in amplifier (PAR model 5208). The response signal was recorded as the X and Y admittance or, equivalently, as a magnitude $|Y|$ at a phase angle θ . To obtain a response spectrum, the frequency of the a.c. perturbation was varied from 3.6 Hz to 100 kHz. Usually, three to four points per decade of frequency were acquired by hand. A computer routine was later added to the growth control program which measured five to ten points per decade of frequency. Either way, the total time required to measure the impedance spectrum was about 15 minutes. During temperature dependence studies of the impedance spectrum, about 15 minutes were allowed for equilibration at the new temperature. Background instrument response to simulated experiments were measured with the substituted calibration circuit and electrical leads positioned as during the experiments.

Observation of transient growth events and fluctuations was not uncommon in our experiments. However, surfaces which grew by distinctly separate events along a background of zero reactivity were very rare. These surfaces were recorded in action by the growth control program described earlier. In a few cases, several minutes of growth events occurring on a very low current background were recorded. Analysis of

these series of growth events showed that the active surface area could be best described as in illustration 9. For studies of these mini-surfaces, we applied small constant potentials with the cell under thermostatic control. Attempts to change temperature while these metastable systems were active were unsuccessful because their period of activity was very short. In systems showing fluctuations in the growth process, some potential dependence studies were attempted. Again, the difficulties of maintaining the activity of these metastable systems prevented significant insight.

Results and Discussion:

In the study of growth in this system, we varied the growth parameters and tried to verify effects that these changes caused. Visual and electronic clues were used to optimize growth conditions in order to produce large, flat single crystal surfaces within the capillaries. These surfaces were four and six sided, corresponding to low Miller index surfaces (100) and (111) in the face-centered-cubic (fcc) system. Usually, side facets of the other orientation were observed bounding a central plane and forming the contact with the capillary wall. The results in the following section describe our observations and conclusions on these close-packed surfaces. The crystallographic orientation of the active and inactive surfaces was not directly obtained within the capillary; rather, visual clues based on surface morphology were used.

The flat crystal planes within the capillary demonstrated three classes of growth. Often, the surfaces behaved like a typical

polycrystalline surface, showing reversible, regular growth and dissolution around the equilibrium potential of silver. A small number behaved as inert surfaces, showing no reactivity over a range of potentials around the silver equilibrium potential. A few surfaces fell between these limits, demonstrating isolated, monolayer and multilayer growth events at small overpotentials. These three classes of growth appear to be tied into the presence or absence of growth enabling sites on the surface. The inert surfaces were characterized by the use of steady-state potential ramps, growth inducing potential pulses, and impedance spectroscopy. The slightly active surfaces were studied through observation of time-dependent growth rates at constant overpotentials.

The experimental conditions used by previous workers to prepare low defect silver crystal surfaces have almost an empirical "recipe" quality^{10,21-29}. Consequently, we investigated a small range of growth parameters around the values traditionally used in order to obtain insight on the physical processes involved. To obtain the filling of any region, the relative horizontal (transverse to capillary) and vertical (along the capillary) growth rates are important. The horizontal growth rate should be much larger than the vertical rate to ensure that capillaries are filled as the crystal grows down the capillary. One of our interests then, was to explore conditions which enhanced the horizontal growth rate with respect to the vertical growth rate. Parameters which were studied in growth experiments were the cell temperature, applied potential, oscillator signal, and solution composition. These are ordered based on total observed effect on growth

behavior. Temperature had the greatest impact on the overall quality of the crystals and capillary filling in these experiments.

Temperatures were varied over the range of 0 to 60°C. The lower limit for cell solution freezing was around -6°C. Since the cell was surrounded by air at room temperature, temperatures above 60°C were not explored because of the large temperature difference between the cell and the ambient. Additionally, the significant changes to observed growth reached limiting values above 50°C. There were very striking differences in the horizontal growth rate between room temperature and about 40°C. These differences were observed in the rate of growth of small isolated surface clusters and in the overall growth response. The current transients describing the microscopic growth processes on the surface appeared sluggish below 20°C and quite fast above 40°C. Actual kinetic parameters for monolayer expansion rates were difficult to determine because of geometric effects. Qualitatively, for the same applied potential, the horizontal growth rates scaled in a linear manner with temperature in degrees celsius. A change of a factor of 2 is significant when observed in the time domain, our method of observation for systems demonstrating growth activity. As long as the temperature was held above 40°C, capillary filling was acceptable. Not all crystals filled the capillary at this temperature, but this temperature marks a point of diminishing returns for further temperature increases. At the high growth rates used in the beginning of the experiments, this temperature kept the growing crystal from becoming a thin strand in the capillary bore. At lower growth rates, it was possible to maintain a filled capillary with lower temperatures.

Applied potential also had a strong effect on growth rates, observed surface morphology and capillary filling. The magnitude of the growth overpotential determines the relative roles of horizontal step expansion in layers and the nucleation of new layers. The competition here is complex but a qualitative comparison is possible. At very low applied potentials, growth by the propagation of a single screw dislocation produces whiskers of 10-50 μm diameter. These potentials are in the range of -1 to -2 mV with respect to equilibrium. At low overpotentials, (-3 to -10 mV w.r.t. equilibrium) the nucleation of two dimensional surface layers can successfully compete with screw dislocation propagation. These potentials were sufficient to obtain moderate capillary filling. At larger overpotentials, growth is rapid within the capillary, and the extent of filling is reduced. This could be due to the tendency to shift from two dimensional nucleation of layers to the three dimensional nucleation of clusters on the surface. During the early stages of growth from the seed crystal, growth was conducted at potentials of -15 to -30 w.r.t equilibrium. Final capillary filling and two dimensional growth studies were carried out with overpotentials of -3 to -10 mV.

Physically, the application of and control of these potentials was not trivial. This was caused by two important factors, capillary resistance and definition of an "equilibrium" potential. Capillary resistance was merely caused by resistance to ionic charge transport along the very narrow capillary bore. A capillary of diameter 76.2 μm , length 0.5" filled with 5.0 M AgNO_3 has a capillary resistance of about 130 k Ω . Any net current through the cell produces a change in the

actual applied potential at the silver/aqueous solution interface by Ohm's law. For a 20 nA current, this potential drop is about 2 mV. The effect on growth kinetics of this voltage drop is maximized at the current maxima of the growth events. The events which we analyze here were observed at lower peak currents and smaller capillary resistance, unlike previous work^{10,21-29}. The other problem observed was that the crystals were about 5 to 7 mV more stable than the silver wire reference electrodes. While the crystal was growing readily within the capillary, the equilibrium potential could be measured by decreasing the overpotential until current ceased to flow. The instability in equilibrium potential could arise from several possibilities. Most likely, changes in the close-packed surface facets' contributions to the exchange current is the cause. On a low defect surface where anodic current (stripping) must be catalyzed by nucleation of pits, one would expect greater stability than on a defect-rich polycrystalline surface. In light of these equilibrium uncertainties, it was only possible to compare small potential changes within an experiment. Overall, comparison of applied potentials between sets of experiments was not possible.

An alternating potential in the form of a square wave was usually applied during the process of growing the crystal down the capillary. Previous workers had used a large ratio between the net growth potential and the peak oscillator potential^{22,23}. Typical signal ratios were in the range of 8:1 for pulse height to applied growth potential. We studied ratios in the range of 2:1 to 10:1 for these signals. Pulse rates of 1 Hz and 50 Hz were studied. The overall effect of the

oscillator was subtle; however, it did prove to be a useful diagnostic tool at 50 Hz as discussed earlier. At the lower frequency, it was much more difficult to isolate the behavior of low activity surfaces since most of their unique kinetics are finished in 10-20 ms. We found that the ratio of the applied square wave magnitude to the growth potential was not very important. However, the absolute magnitude of the pulses had to be above 100 mV peak to peak to suppress screw dislocation propagation and encourage capillary filling. By allowing potentials large enough to nucleate a new layer or a pit, the pulses can decrease the significance of screw dislocation propagation at low overpotential. The amplitude of the pulses required to accomplish this will depend of the temporal duration of the pulse. For the 20 ms wide pulses here, 100 mV peak-to-peak was sufficient.

Cell solution composition was briefly investigated. While retaining a constant high concentration of AgNO_3 , both the oxygen content and the solution pH were varied. Solutions were deoxygenated before experiments by bubbling dry nitrogen for up to 10 minutes. After assembly, the cell was sealed to prevent contamination by oxygen. No differences were observed in crystal morphology or extent of capillary filling between experiments where the solution was deoxygenated and experiments where the solution was untreated. The reduction potential of oxygen in solution was negative enough so that oxygen reduction was not observed, preventing background currents in these experiments. The effects of low to moderate pH were studied in later experiments. High pH conditions were avoided because of the tendency of some silver crystalline faces e.g. (110) to form silver oxide in alkaline

solutions^{14,18}. The pH was lowered by spiking with a solution of high purity perchloric acid. Again, no striking differences were observed over a range of solution pH from 3 to approximately 7. During the course of experiments, the low pH solutions were used to provide a controlled and low hydroxide ion concentration.

The observation of nucleation and growth on inert surfaces generally consisted of two techniques. Short timescale experiments provided information on the limiting kinetic processes and long timescale experiments yielded equilibrium measurements of growth onset. In these long timescale experiments, growth effectively "turned-on" over a window of a few millivolts. In our work, the activation of an inert surface could be classified as a catastrophic event occurring at a large overpotential. This differs from previous work where fluctuations were seen in growth at lower applied overpotential^{10,26,27,29}. Two possible models which can explain our observation of catastrophic events follow. One explanation may be that the surface is contaminated, resulting in a deactivation of surface sites. Another explanation consistent with previous work is that growth within the capillary has eliminated a class of surface sites which are active at low overpotential. In either case, it is completely reasonable to analyze our results at these two timescales to obtain kinetic and energetic data on these inert interfaces.

Illustration 10 shows results from a pair of runs of the long timescale experiment. The top curve is a plot of the physical limit, $V = iR$, where R is the capillary resistance (109.7 k Ω). At large potentials, both of the experimental curves approach this limit. One of

the experimental curves is the growth of a polycrystalline wire limited by a resistor equal to the capillary resistance. The other curve is the growth of the inert surface. On this logarithmic current scale, the observed growth is "zero" until some leakage charge begins to pass. These charges are fractions of a monolayer and may reflect the adsorption and charge transfer of precursors to growth. Possible precursors would be silver adatoms and their surface concentration should increase with potential. Once the potential exceeds a critical value, the growth current makes a sharp transition to the physical limit.

The growth of the polycrystalline wire, on the other hand, does not show onset behavior. These experiments were conducted with the same solution, in a comparison of the working electrode (crystal in capillary) and the reference electrode. These two different results would imply that surface contamination from solution species is not playing a significant role in the observation of inert behavior. For kinetic analysis, we are able to acquire a single data point, the onset potential and an estimation of the nucleation rate at this potential.

The large amplitude pulse experiments to study limiting nucleation rates were simple two-step experiments. From an initial potential where no current was flowing, a 50 to 300 mV pulse was applied. After a short period, the potential was returned to the initial potential and the current was recorded to look for growth triggered by the pulse. The slow pulses between 1 and 50 ms long were generated by the controlling computer and shorter pulses were made with the help of a waveform generator. Large potentials are applied to form surface precursors

which combine to form clusters on the surface. When a cluster is large enough to continue its growth even at the lower potential, a new phase has successfully nucleated and the cluster will grow and produce a current. By stepping to arbitrarily large potentials, we attempt to measure the absolute rate of cluster formation, independent of surface precursor issues. For the range of potentials that we used, the typical pulse width that produced a growing cluster on more than 50% of the pulses was 1-5 ms. Extending this to an arbitrarily large potential, the limiting rate is on the order of 10^{10} per second $\cdot$ cm².

The two results outlined above can be applied to nucleation theory to determine energetic information relevant to the solid/liquid interface. A simple derivation from an equilibrium view of the surface gives the following expression for the rate of nucleation of a new two-dimensional phase of height h^8 . (See appendix B for an outline of the derivation)

$$A = A_0 \cdot \exp \frac{\pi \frac{v}{h} \cdot \epsilon^2}{[\frac{v}{h} \cdot \sigma_{13} - ze\eta]kT} \quad (2),$$

where A_0 is the limiting rate of nucleation in nuclei per second $\cdot$ cm², ϵ is the edge energy of the new phase in J/cm, η is the overpotential, and σ_{13} (in J/cm²) is the surface tension between the substrate and the new phase. For an experiment that probes the nucleation of a like phase on a clean, defect free surface, this surface tension term will be identical to zero. The surface energy term can be stabilizing or destabilizing for a non-ideal surface and unsymmetric systems. Taking

our results to be representative of the former, we can calculate the edge energy of a two-dimensional cluster of silver. We obtain $\epsilon = (2.7 \pm 0.2) \times 10^{-13}$ J/cm. The error bar is small because the nucleation rate is explosive with potential, fixing ϵ to a high degree even with significant experimental uncertainty. This result is similar to results obtained by Budevski et. al. in silver screw dislocation propagation experiments $\epsilon \sim 2.1 \times 10^{-13}$ J/cm²¹ and $\epsilon \sim 2.7 \times 10^{-13}$ J/cm¹⁰.

Illustration 11 shows the onset data point and its uncertainty and the model curve for our ϵ and set σ_{13} equal to zero. The vertical axis in this graph is the logarithm of the nucleation rate; our onset data is a rate of about one event on the surface in 10 seconds. At lower applied potentials, the model curve based on this data falls sharply, producing very long time periods, $> 10^{10}$ seconds, between nucleation events on these inert surfaces at applied potentials less than 8 mV.

To place our results in the context of previous work, we propose that nucleation rates are enhanced by the stabilization of surface clusters at defect sites. Previously published results on silver are schematically represented by the ellipse in the upper left of the graph in illustration 11. A line of the model equation (2) with our determined ϵ and $\sigma_{13} = -4 \times 10^{-2}$ N/m passes through this region. This stabilization energy is a 5% change in silver's bulk surface energy, yet it produces a rate enhancement of many orders of magnitude. These results provide new information regarding the microscopic balance which affects nucleation and growth. The interpretation of growth through an energetically distributed active site model is also being pursued by

Deutscher and Fletcher in the modeling of growth on assemblies of electrodes⁷.

The inert silver interface also provides an important starting point for other investigations of interfacial properties. The key to this is the low chemical reactivity of the surface. Impedance spectroscopy is a useful tool for examining interfaces. An impedance spectrum of one of these inert silver surfaces is shown in illustration 12. We have acquired these data over several temperatures and analyzed the experimental response in terms of physically reasonable processes at the solid/liquid interface. The low chemical reactivity of these silver crystals greatly assisted in parameter fitting and analysis. As measured, the spectra contained both experimental signal and instrumental distortion. The instrumental distortion was corrected via calibration circuits with known response. Calibration circuits were designed to approximate the response of the experiment based on less distorted parts of the impedance spectrum. The differences between the observed response and the calculated response of the calibration circuit were used to correct the instrumental distortion. If required, this corrected data set was used to create an additional model circuit of greater accuracy or sophistication. The validity of this technique was checked through the measurement of a complex, yet known, test circuit. Later versions of the electronics were designed to reduce instrumental distortion. Studies with these improved electronics were done to verify that our experimental model circuit was appropriate. As this was found to be the case, experiments over a wide range of temperatures were not repeated.

The interfacial admittance is shown in illustration 12 as logarithmic in magnitude and linear in phase angle (secondary vertical axis) versus the logarithm of the perturbation frequency. When using a range of frequencies this form of plot is significantly more informative than the more traditional plot of imaginary impedance vs. real impedance. We are able to model the response of the inert interface over the temperature range of 0 to 45°C with the following equivalent circuit:

In order to interpret the admittance data, the various elements of the circuit above are linked to physically relevant processes at the interface. The series resistive term R_u corresponds to the "uncompensated" resistance in the capillary to charge flow. The interface itself is modeled by three parallel processes; charging the electrical double layer at the solid/liquid interface (C_{dl}), adsorption of a species at the interface accompanied by charge transfer (R_a , C_a), and net charge transfer by chemical reaction (R_{ct}). Table 2 shows best fit quantities to most of these values obtained over the temperature range studied. The data in the table were determined by fitting the data based on analytical response of the model circuit. The high frequency limit of the admittance allows quick determination of the

T / °C	R_u / Ω	R_a / Ω	C_a / nF	C_{dl} / nF
0	1.132×10^5	3.98×10^5	1.256	0.593
5	1.121×10^5	4.06×10^5	1.118	0.745
10	1.115×10^5	4.46×10^5	1.117	0.912
15	1.114×10^5	4.93×10^5	1.020	1.102
20	1.113×10^5	5.74×10^5	0.931	1.322
25	1.110×10^5	7.36×10^5	0.836	1.556
30	1.102×10^5	1.00×10^6	0.756	1.779
35	1.099×10^5	1.97×10^6	0.808	2.064
40	1.092×10^5	2.52×10^6	0.872	2.372
45	1.082×10^5	2.33×10^6	1.230	2.612

Table 2. model circuit values from admittance experiments on an inert silver interface, perturbation magnitude 33 μ V, overpotential -4 mV.

series resistance because it is the dominating circuit element. The rolloff point and frequency at phase shift of 45° provide estimates for C_{dl} . The low frequency portion of the admittance can be fitted to a sum of C_{dl} and C_a .

From these starting estimates, the experimental data were fit by a graphical, iterative process. The uncertainty in the R_u values were fairly large due to the instrumental distortion and corrections applied. The error here is a systematic shift rather than a precision error between the results at individual temperatures. The largest uncertainty in the determined values above is found in the R_a values. These numbers are valid to one figure since their impact on the observed admittance response was small. The R_{ct} values were all quite large yet detectable

through the low frequency limit of the phase angle in the admittance spectra. Limits can be placed on the maximum R_{ct} value based on the steady state potential increase experiments. We estimate $R_{ct} \leq 2.5 \times 10^{10} \Omega$ for our crystal with surface area $4.5 \times 10^{-5} \text{ cm}^2$. This is an exchange current that is 10 orders of magnitude smaller than a typical polycrystalline electrode. The uncompensated resistance term varied consistently with temperature. Converting the values to concentrations revealed values consistent with the molar conductivities of Ag^+ and NO_3^- . Solution diffusion coefficients from these conductivity values were on the order of $10^{-5} \text{ cm}^2/\text{s}$.

Measurements of the double layer capacitance (C_{dl}) are usually interpreted in terms of a series of three components³¹. These components are the electronic and ionic contributions (C_{el}), the contribution from rearranging water dipoles at the interface (C_D), and the diffuse layer contribution (C_{dif}). In these concentrated electrolyte solutions, the capacitance for the diffuse layer is effectively infinite. Our experiments are done on a silver surface around the equilibrium reduction potential, placing the surface at a potential very positive with respect to the point of zero charge. In this case, the capacitance from the electronic and ionic contributions should be much larger than the capacitance from dipole reorientation. Therefore, a series combination of these three components is dominated by the capacitance caused by the water dipoles:

$$C_{dl}^{-1} = C_e^{-1} + C_D^{-1} + C_{dif}^{-1} \approx C_D^{-1} \quad (3).$$

In light of this, our results show the expected response with temperature, namely, the capacitance C_{dl} increased with increasing temperature. Measurement of the dipole contribution to the interfacial impedance has historically been hindered by the presence of other faradaic processes (usually net charge transfer). These inert interfaces provide negligible faradaic reactions at high surface charge, creating ideal conditions for measurement of C_D . Previous direct measurements of this quantity on low-defect structureless metals has been restricted to the liquid metals³⁵.

A simple relation correlates the dipole capacitance per unit area to the effective dielectric function of the interface:

$$\epsilon = \frac{C_D s}{A \epsilon_0} \quad (4).$$

This is the result for a parallel plate capacitor with thickness s and area A ; ϵ_0 is the permittivity of free space (8.85×10^{-12} F/m). Since the closest approach of ions sets the boundary of the dipole capacitance region, the hard sphere diameter of water is a good approximation to s . A plot of the temperature dependence of this quantity is shown in illustration 13. The dielectric constant of the interface at low temperature is very low in comparison to bulk water. This value approaches the limit of the polarizability of a "frozen" water molecule at the interface. At room temperature, the experimental dielectric constant is 10 while the bulk value is 78 (ref. 36). Our data suggest that the reorientation of the first layer is an activated process. The enthalpy of reorientation we measure is $\Delta H = 24.5$ kJ/mol. This term should reflect a combination of water-water molecule interactions

through hydrogen bonding and water-metal bonding. The majority of this reorientation energy is from this second term.

The adsorption of a species at the surface was included in the model in order to obtain the best fit to the admittance spectra. We assign the adsorption parameters extracted from the data to the adsorption of charge neutral silver adatoms. These adatoms would be free to move along the interface and desorb with accompanying charge transfer. Changes in surface concentration of these species due to a perturbation in potential appear as a capacitance C_a and their rate of formation will produce a resistance R_a in series with this capacitance. For full charge transfer (one electron lost per adsorbed atom), the surface coverage of silver adatoms Γ_{Ag^0} is related to the capacitance by;

$$\Gamma_{Ag^0} = \frac{RTC_a}{AF} \quad (5)$$

near the equilibrium potential. R and T have their usual meanings, A is the surface area, F is Faraday's constant and the units of Γ_{Ag^0} are mol/cm². A plot of the natural logarithm of this quantity against $1/T$ is shown in illustration 14.

At the higher temperatures, the fits to the data were not as strongly dependant on the adsorption components, producing less confidence in the values from 35°C to 45°C. The coverage of the species on the surface is fairly low at room temperature, $\theta = 2.7 \times 10^{-3}$, or one adatom per 400 surface atoms. The adspecies formation energy over low temperatures is $\Delta H = -8$ kJ/mol. For a silver adatom, this energy

reflects the both the loss of solvation, and stabilization by surface-adatom bonding. The reaction of adatom formation as it is discussed here is different from the bulk deposition of silver, which may or may not be preceded by the formation of a silver adatom. The physical difference between deposition and adsorption at the interface is that deposition of an atom always results in a site for potential future growth. When a species adsorbs at a surface or interface, an adsorption site is occupied and will not be released to another species until the adsorbing species deposits or desorbs.

Our experimental study of the interfacial impedance of these inert interfaces represents the application of traditional impedance characterization to a new type of system. There has been previous impedance characterization experiments conducted on silver electrodes, however they were conducted at only at room temperature and in the presence of large faradaic currents^{15,17,19}. This new, inert, system has allowed some modification of the typical approach. Due to the negligible net faradaic reaction of growth at the surface, we were able to measure the interfacial admittance over several decades of frequency. This wide frequency range of data increases our confidence in the ability of the model circuit to describe the relevant processes at the interface. In making conclusions regarding dipolar orientation energy and silver adatom formation we had to assume that their signatures were appearing in C_D and C_A respectively. However, these are the most sensible assignments based on the physics and chemistry of the surface under study.

When active, the silver surfaces demonstrated a range of response characteristics depending upon cell potential, cell temperature and surface morphology. The most interesting and tractable results we observed in the growth of these silver surfaces were when the growth shifted from regular growth (small normalized deviation of current) to periodic growth (large normalized deviations). Interpretation of the net current flowing through the cell is simple; it is always related to a reaction rate multiplied by an active site number. Complexity appears for systems which have a number of site classes, each with a different rate of reaction. In general, the growth current can be expressed as;

$$i \propto \sum_j k_j N_j \quad (6)$$

with k_j being the rate of reaction and N_j being the number of sites of a particular class, j . This general expression describes typical growth, a sum of a number of microscopic processes producing a total reaction rate which is an average of the individual rates weighted by the number density of sites. Since a large number of sites can contribute to the growth, the observed current is regular and has small fluctuations. When a limited number of classes are involved in growth, it is feasible to correlate the instantaneous current with the microscopic rate of reaction k_j . For example, the growth of a single isolated two-dimensional cluster will produce a growth current proportional to the peripheral length of the cluster. The periphery of the cluster provides the potential future growth sites, so as the cluster expands, the reaction rate increases;

$$i \propto knL \quad (L = 2\pi r \text{ for a circular growth front}) \quad (7)$$

where L is the peripheral length and n is the number of active growth sites per unit length of periphery. Previous work has demonstrated the utility of such an interpretation²⁶. Essentially, the current resulting from a simple growth event can be used to define the geometric constraints involved in the event. We were able to observe growth events that corresponded to a fraction of a monolayer in total coverage (4×10^9 atoms), describing activity on a subset of the entire surface within the capillary. From a simple geometric interpretation of equation 7, we were able to determine the time dependent peripheral length from the current for a constant k and locate the site of initial cluster formation.

A typical growth event which we observed is shown in illustration 15. Each growth event begins with a linear region of growth. The slope of this region is identical to other growth events appearing in the same experiment. This portion of the growth corresponds to a cluster expanding freely on the surface. In our experiments, the growing clusters are bounded on one side by the edge of the crystal next to the capillary wall. Illustration 9 shows the configuration; the cluster begins growth at nucleation site N and expands with rate v ($v = kn$). When this expanding layer strikes the edge of the facet, the active peripheral length decreases as long as spillover onto the other facet does not occur. Since the cluster's peripheral length is decreasing, the current flowing through the cell drops while the expanding layer

completely covers the facet. The solid line in illustration 15 is a best fit model curve based on this simple geometric interpretation, assuming a geometry as in illustration 9. The cluster appears to grow as a circle, under kinetic rather than thermodynamic control. From the growth events, the isotropic rate of expansion v is determined from the initial linear region. The distance h in illustration 9 is calculated in two ways; from the capillary radius and the charge passed in the growth event and from the time required for the cluster to reach the facet edge at growth velocity v . This provided a self-consistency check of the geometric interpretation. For a given transient, the agreement in these factors was good to a few hundred nanometers (about 5% of the total distance, h). The origin of the cluster is determined as a shift from a mirror plane of symmetry by the fit of the model to the tail of the transient. A self-consistency check can also be applied to this location by interpretation of a series of experiments and will be described later in this chapter.

Of course, this geometric interpretation was selected from many possibilities. In fact, model curves for a number of possibilities were calculated. One section of chapter 2 presents a very important example of the growth of a circle into an elliptical boundary. Along with the consideration of other possible models, extensive data from growth events of slightly varying geometries were applied in the determination of the best description of the surface morphology. A longer portion of the time series which contains the data in illustration 15 is presented in illustration 16. During this experiment, sets of small events are separated by large events. Each of these large events amounts to the

passage of several monolayers of surface charge. The large events also produced changes in the size of the surface region active in the small growth events. From these data, a model of the surface was constructed, a pictorial representation is in illustration 17. The side view in this illustration shows in the shaded region the material added in a large growth event and its effect on the length h . Optical observations of silver crystals growing in capillaries confirmed the presence of this type of surface morphology. In illustration 18 the small events appear in a regular fashion. Overall, we observed this type of behavior quite frequently even though it has not been discussed in previous work in this system. Previous analyses of microscopic growth events on silver surfaces within capillaries have described events which appear as a stochastic time series. The events in those previous studies^{26,27} were stochastic in both arrival time between events and in the apparent location of the nucleation events. The presentation of stochastic observations was used to establish that the surfaces were defect free.

On the other hand, we find that the surfaces prepared in capillaries contain lower defect densities than free standing single crystals yet are far from defect free. A signature of the presence of interfacial defects are temporally and spatially deterministic events as in illustration 18. In fitting sets of transients like illustration 15 we observed two important points. Firstly, all of the nucleation events occurred at approximately the same location. Secondly, when observing several microfacet sizes, h , the time between growth events varied in a regular manner. These two observations of periodic growth represent significant departures from the reported behavior of this system.

Illustration 19 shows a summary of the fitted results over several minutes of observation. The values for each h and τ (waiting time) are calculated by averaging the fitted values for each set of small events. The waiting time τ was extracted from the growth events by measuring the time between the peak of a growth event and the time to the start of the next growth event. The data in this illustration are from the 20°C data, the data acquired at 50° also showed this linear behavior. The strong linear relation between facet length and square root of time implies a relation of the form:

$$h^2 = C\tau \quad (8).$$

This is the expected result when transport via surface diffusion is the rate determining step in the nucleation process! The diffusion length here is identical to the length from facet edge to nucleation site. At very short times, the intercept of the plot is another measure of the location of the active nucleation site. This was an unexpected result since the defect site that catalyzes the formation of critical clusters appears to rely upon the arrival of surface species in the initial stages of cluster growth. In summary, these experiments observe nucleation at a single site within our ability to locate it via geometric analysis, and the arrival times of these nucleation events appear to be related to surface transport.

The combination of two non-linear processes, mass transport and nucleation, have produced another chemical oscillator³⁷. Solution diffusion of reactants has been eliminated as a candidate for the

limiting mass transport mechanism by the high concentration of silver ions and their mobility. A fluctuation in the local concentration created by the sudden passage of the charge in the transients would be replenished in a few milliseconds. We turn to surface-based mass transport to provide the reactants for a nucleation event. Other surface regions should have some equilibrium coverage of adsorbed silver atoms as measured by the interfacial impedance studies. We also know from those studies that the rate of formation of the adsorbed species is very slow. Using the impedance results for C_a and R_a at 20°C, the rate of adatom formation is so slow that an equilibrium concentration on a small, narrow surface region could be established faster by diffusion from a nearby large source.

To convert the observed slopes in the h vs. $\tau^{1/2}$ plots into a surface diffusion coefficient, the experiment was computationally modeled. The model details and an extensive discussion of the calculation are in chapter 2. The simple diffusion equation³⁸;

$$\langle x^2 \rangle = 2D_s t \quad (9),$$

could not be applied to the observed results because this system is driven by a concentration gradient. Each layer that grows across the interface depletes the surface concentration of adsorbed silver atoms. Diffusion from the facet edge begins when the new layer comes in contact with the bounding edge. The computational model treated the "rest of the crystal" as a source of surface concentration as determined by the interfacial impedance work. After each growth event, hypothetical

adatoms were allowed to diffuse from the equilibrium source until they were detected at the nucleation site. The microfacet region constructed a "time-of-flight" experiment where adatoms depart from a source, diffuse across a region of known length, and are detected at a sink by the growth event which they cause.

The simulations provided correction factors that were used to convert the linear relation between the region length and the diffusion time to a diffusion coefficient of the usual sense. Table 3 presents our results and a comparison to two previous molecular dynamics calculations for a close-packed fcc metal surface in contact with a vacuum^{39,40}. For silver, previously available techniques for measuring metal surface self-diffusion coefficients (e.g. field emission microscopy^{41,42}) have not been practical. This is the first direct measurement of a self-diffusion coefficient for the surface of silver exposed to any medium. It is also the first direct measurement of diffusion of metal atoms at the metal/water interface.

System	$D_O / 10^{-4}$ $\text{cm}^2 \text{ s}^{-1}$	$E_a /$ kJ mol^{-1}	$D_S / (20^\circ\text{C})$ $10^{-7} \text{ cm}^2 \text{ s}^{-1}$	$D_S / (50^\circ\text{C})$ $10^{-7} \text{ cm}^2 \text{ s}^{-1}$
Ag(111)/H ₂ O	2.7	19	(1.2 ± 0.3)	(2.5 ± 0.9)
fcc(111)	3.4	12		
fcc(111)	5.3	13.3		

Table 3. Comparison of experimental results and molecular dynamics results scaled to silver surface self-diffusion.

For our two temperatures, it is possible to calculate an activation barrier and intercept for a thermally activated diffusion

process;

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (10).$$

We calculate a significantly larger activation barrier than the molecular dynamics simulations. Since the molecular dynamics calculations have provided good agreement with other experiments on fcc close-packed surfaces in ultra-high vacuum, a portion of the disagreement could be due to the role of liquid structuring at the interface. From the interfacial impedance studies, we predict a moderate reorientation energy for the water dipole. The activation barrier to silver diffusion is a bit smaller, suggesting that along with the metal-metal interaction normally present, the water layer is slightly distorted by the passing adatom from its equilibrium position. This conclusion is consistent with work suggesting that structured water overlayers on metals are arranged in a loose hydrogen-bonded network⁴³. These experiments suggest that the presence of water at the surface mildly perturbs the energetics of normal surface diffusion. Additional results at other temperatures are not reported due to the difficulty of these experiments. Additional experiments to measure surface diffusion around these temperatures would be nice, but their utility is limited since the experimentally available window of $1/T$ is narrow. For a narrow region of $1/T$, the determined activation energy and intercept will always have a high uncertainty.

Summary:

The study of inert and slightly active surfaces allowed determination of quantities which have previously been experimentally problematic. We have observed the reorientation of water molecules through impedance spectroscopy. Nucleation rates for inert surfaces and the observed experimental results of multiple workers have been placed in a context of surface free energy terms and defect site stabilization factors. Finally, the impact of surface diffusion on microscopic growth processes were observed. From temporal analysis of isolated growth events, surface diffusion coefficients for silver surface atoms were determined. One interesting direction for further study on this system would be the use of defect site location information of as a guide to the study of the defect surface structure. A map of several sites with different cluster nucleation rates could be used to correlate surface structure with energetics and reactivity.

illustration 1:

Control signal generation circuit. At left is the square-wave oscillator subsystem, to the right is the adjustable precision voltage circuit.

illustration 2:

Two buffer circuits. At left is a fixed gain non-inverting amplifier used to monitor the applied potential. The adjustable amplifier raises the current signal to high levels, and performs time averaging of the signal.

illustration 3:

Circuit design for a simple three-electrode potentiostat. The useful current range goes down to pA, with current gain at pin 7 of $20 \times 10^6 \text{ V / A}$.

illustration 4:

High-speed two-electrode electrochemical cell control circuit. The useful current range goes down to 100pA, with current gain at pin 7 of $10 \times 10^6 \text{ V / A}$.

illustration 5:

Sketch of experimental cell. The long commercial capillary and sealed reference electrode are shown here. The exploded view shows the capillary bore and silver crystal growing within.

Initial Shape

Filled with Wax

Final Shape

illustration 6:

Preparation of short capillaries. At left is the shape resulting from rotating within the torch flame. The capillary is filled with black wax to protect the bore while polishing. The end is polished until a uniform diameter tube is present at the end of the capillary and then the wax is removed.

Thermal Control Apparatus:

Copper tube coil

Plexiglass Jacket

illustration 7:

Two configurations used for thermal control. The copper coil was wrapped with cotton gauze for additional insulation. For both configurations, cotton gauze was placed over the top part of the cell.

illustration 8:

Sketches of oscilloscope traces observed during growth. A net overpotential towards growth produces the asymmetry in the peak current values. The shape of the knee was exaggerated as the surface reactivity decreased.

illustration 9:

Geometry of active portion of surface during a set of experiments at 20°C. N denotes the site at which all growth events began. The distance of the microfacet edge to the active site is d while the maximum distance from the capillary wall to the microfacet edge is h . Modeling of growth events as isotropically expanding circles allows calculation of the expansion rate, v and the nucleation site N from the experimental data.

illustration 10:

Steady state current response at 45°C for a silver wire and an inert silver surface. The physical limit, Ohm's law $V = iR_u$ ($R_u = 110 \text{ k}\Omega$), is included for comparison.

Log of Nucleation Rate vs. Overpotential

illustration 11:

Nucleation rate versus overpotential. Solid curves are models calculated at two stabilization factors σ_{13} . The experimental point with error bars is drawn from the data shown in illustration 10. The model curve through this point uses cluster edge energy $\epsilon = 2.7 \times 10^{-13}$ J / cm and $\sigma_{13} = 0$. The elliptical region at the upper left bounds previously reported random nucleation and growth events. The model curve through these data is calculated with cluster stabilization term $\sigma_{13} = -4 \times 10^{-2}$ N / m.

illustration 12:

A plot of the admittance at one temperature and the best fit model curve. Cell admittance is the reciprocal of the cell impedance. The experimental data has been corrected for instrumental distortion as described in the text. Perturbation magnitude 33 μ V and applied potential -4.0 mV. The low frequency limit illustrates the inert nature of the surface, the falling admittance magnitude indicates a negligible d.c. conductance. At high frequencies, the cell response is dominated by the capillary resistance R_u .

illustration 13:

Interfacial dielectric constant (ϵ) determined from the double layer capacitance C_{dl} . Values assume a parallel plate capacitor with thickness of the water hard sphere radius. This distance approximates the distance of closest approach of ions within solution. The interfacial dielectric constant at 25°C is significantly less than the bulk value of 78. Least squares line shown through the data, $r^2 = 0.996$.

illustration 14:

Adatom coverage determined from adsorption capacitance plotted against reciprocal temperature. High temperature results were hindered by signal resolution in the admittance data. Activation energy from lower temperature least squares fit is $\Delta H = -7.6 \text{ kJ / mol}$, $r^2 = 0.903$.

Single Growth Event and Model Curve

illustration 15:

Single growth event and best fit model curve. Solution temperature 20°C, overpotential $\eta = -1.0$ mV, 1 kHz data sampling rate. Total growth charge 0.582 nC, expansion rate $v = 1.8 \times 10^{-2}$ cm s⁻¹, microfacet size $h = 8.2$ μ m, assuming Ag(111) surface packing density. Several of these small events were observed in a regular sequence.

illustration 16:

Long time series, 30 seconds, showing a mix of large catastrophic events and the small regular events. The large events consist of 40 to 60 times greater charge passed than the small events. The period change between the regular events caused by the catastrophic events is quite clear. Growth conditions as in illustration 15.

illustration 17:

Sketch of active surface inferred from the experimental data in illustration 16. A large Ag(100) crystal surface, square grid, occupies the major portion of the capillary. The sides bound small facets which are bounded by the circular capillary boundary. One of these small (111) surfaces is the location of the small regular events. For the data shown in illustration 15, the nucleation site is denoted by N in this figure. The side view shows a possible mechanism by which the catastrophic events can increase the microfacet size h . Scale exaggerated for clarity.

illustration 18:

Subset of illustration 16 showing a regular series of five growth events. The small event appearing around 1000 milliseconds into the plot is from activity on one of the other small facets exposed to the solution, see illustration 17 a). Growth conditions here are as in illustration 15. Each of these growth events occurs on a similar surface geometry with a microfacet size h . The waiting time discussed in the text is the time delay between the contact of a growing layer to the microfacet edge (peak of growth event) to the start of the next growth event.

Microfacet Size vs Square Root of
Waiting Time

illustration 19:

Summary of deterministic growth observations from approximately 60 growth events at $T = 20^{\circ}\text{C}$. Individual series like illustration 18 are compiled together by averaging waiting time and microfacet size of 5 to 10 growth events. The least squares fit line is shown; $r^2 = 0.998$. The non-zero vertical intercept provides an independent measure over the data set of the distance $\langle h-d \rangle$ as defined in illustration 9. The 95% confidence range for this intercept contained the typical value used to make the best-fit model curves as illustration 15.

CHAPTER 2

COMPUTATIONAL MODELING OF GROWTH IN SIMPLE SYSTEMS

Introduction:

Geometric analysis of microscopic growth events has been used previously to locate initiating sites and determine kinetic parameters^{26,27,29,44}. Previously published work has determined analytical and approximate descriptions of expected total growth rates given an initial configuration and other relevant parameters^{7,45-50}. Although we focus here on measuring total growth rates at the interface through electrical current, there are other methods of monitoring surface and interfacial reactions. The discussions here and elsewhere can be extended to any technique that is capable of observing a total rate of reaction at the surface or interface. When the dimensionality of a chemical reaction is restricted to that of the surface, geometric interpretations of the total rate of reaction can be very powerful tools. It is possible to derive the expected time-dependent total reaction rate for a given configuration. Additionally, inversion of the total reaction rate vs. time can be accomplished analytically in special cases to extract the geometric configuration. These derivations and inversions for the case of two-dimensional growth have been restricted to very simple cases for algebraic reasons.

The most simple case of two-dimensional growth, the growth of a circular phase upon a circular substrate, has been treated by previous work. Analytical results for simple boundaries and single clusters⁵⁰

have been derived as well as approximate results for multiple numbers of clusters⁴⁵⁻⁴⁹ and, recently, for multiple electrode arrays⁷. The observable quantity is a total reaction rate as a function of time. These model calculations are an effort to convert this observable quantity into parameters which describe issues involved in microscopic growth. For the case of a single circular cluster, the expected total reaction rate as a function of time is easily derived for boundaries of a circle, square, or other simple polygons. The time-dependent reaction rate depends on both the microscopic expansion rate of the cluster and the initial location of the cluster. For these simple geometries, it is possible to invert the entire time series of the reaction rate for a growth event to extract an initial location. However, the analysis of time series of this type is usually performed through analysis of critical points in the time series. Analytical attempts have so far failed to determine the time-dependent total rate of reaction when the boundary is an ellipse. This is due to the complexity of the model when expressed as a completely general two-dimensional problem.

We have applied computational simulation to this problem and to the diffusion of species under arbitrary boundary conditions. For the growth of a circle into an ellipse, a number of techniques were applied with varying degrees of approximation. Along with simulations of the expected reaction rate, algorithms were developed to automate analysis of data. These algorithms used the simulated growth curves and extracted critical points for a number of simulated growth events. The set of critical points was then used to calculate the eccentricity of the original boundary and the initial locations of the growth events. A

subset of the simulation of the growth of a circle into an ellipse is the modeling of the time series which we observed experimentally (see chapter 1).

Simulations of random walks were run on a computer to study both single event arrival times and statistically averaged quantities. The random walk simulation probed cases where diffusion from an equilibrium region fills a population-depleted region. This chapter is divided into three sections to cover these subjects. The first section presents a discussion and simulations of a circular cluster growth into an elliptical boundary. The second section shows how the experimental time series were modeled. The last section presents our techniques and results in the random walk simulations.

Section 1: Circle into Ellipse

The ability to analyze a growth event at a surface or interface and extract kinetic and positional parameters is very important. The microscopic expansion rate of a cluster can be a tool for the investigation of the mechanism of the growth reaction. Very simple experiments, or at least conceptually simple experiments, can be employed to determine how microscopic kinetics and mechanism are affected by factors such as temperature and supersaturation. Positional parameters are useful in the study of growth events in many ways. For example, series of events can be studied for positional correlation. Strong positional correlation between events can indicate that specific sites at the surface or interface are promoting nucleation. Even the

spatial propagation of the nucleation promoting site can be followed when a small number of sites are active. Another use of the nucleation position information is as a guide for subsequent high resolution surface probes. This potentially enables atomic resolution of a growth promoting site if the growth experiments can be conducted in the presence of an atomic force microscope⁵¹ or scanning tunneling microscope⁵². Previous analyses of growth of silver thin films have shown at least moderate agreement between experimental and geometric models, and have demonstrated potential for further study in location and structure of nucleation promoting sites.

The agreement of the experimental results and simple models has been largely due to the experimental conditions. Under the growth conditions used in these solution phase experiments, the growth is under kinetic rather than thermodynamic control. Kinetic control causes the flat two-dimensional clusters expanding on the surface to take a circular shape and grow with an isotropic expansion rate. As the clusters approach boundaries, they continue to behave like circles and the interaction between the new layer and the wall remains simple. When the system under study follows these approximations, simple geometric models as discussed here and elsewhere are valid.

Positional analysis of growth events by geometric interpretation of total reaction rates is restricted by symmetry in the growth system. The total reaction rate of an isolated growing cluster can be expressed as a function of a microscopic rate multiplied by the total cluster peripheral length. Initial positions on the substrate which produce identical peripheral lengths as a function of time are impossible to

distinguish. Illustration 20 shows two examples, that of a circular cluster growing within a rectangle and within a circle. For a rectangle, all the positions where growth initiated are mapped onto one quadrant of the total surface. For a circle, the symmetry of the system makes the problem one-dimensional, producing a map of radial positions and no angular information. For positional analysis, mapping the data into a quadrant is obviously useful. Radial information has been used to check for signs of non-random nucleation²⁶; however, the power of this interpretation is limited. Single crystal planes within a circular capillary will produce an elliptical boundary if the surface normal does not point in the same direction as the capillary bore. The eccentricity of this ellipse breaks the circular symmetry and allows mapping positional information to a quadrant of an ellipse. Therefore, for positional analyses of growth events occurring on substrates within circular capillaries, a little misorientation can be beneficial.

Previous analyses of growth events have applied special regions of growth events, critical points, to distill geometric information from the data⁴⁴. The analysis process with this technique has two major steps. Several of the observed growth events are pulled at random from a data set of potentially hundreds or more events. The pulled growth events are studied for characteristic features. Useful regions are periods of linear growth, regions of discontinuity (critical points), and overall curvature during the growth event. The characteristic features are used to develop a self-consistent geometric model for the boundary and the growing phase. Once a reasonable geometric model is

developed, it is possible to completely describe all the growth events in the data set by reducing the data to critical point information.

Data set reduction by critical point analysis is important in these systems due to the number of points which are recorded in a growth event. With typical data acquisition rates, a single growth event occurring on a $5 \times 10^{-4} \text{ cm}^2$ silver crystal surface can create a data curve with 400 to 40,000 raw data points. To obtain a thorough analysis of a system many (tens to thousands) of these growth transients should be recorded and analyzed. For systems where analytical inversions from reaction rates to geometric information exist, it would be very computationally intensive to handle every data point. The best argument for data set reduction via critical point analysis, however, is that it works very well. Once a geometric model is shown to be descriptive of a system, any observed growth event may be simulated with a small number of input conditions. The key to this analysis is the conversion of the critical points as extracted into initial position and kinetic parameters.

As an brief example, the simulation of a circular cluster growing into a circular boundary will be presented here. Illustration 21 shows a new circular layer in various stages of growth on a circular boundary and the resulting growth current signal. There are three critical points in the growth reaction. The first is the start of the growth event. The second occurs when the cluster makes its first contact with the boundary. The final critical point occurs when the substrate is completely covered. For this curve, two critical times, t_1 and t_2 , are defined as the time from the first critical point to the second and

third critical points respectively. The initial slope of the growth event is geometrically related to the microscopic expansion rate by (the total growth current gives reaction rate);

$$\frac{di}{dt} \propto 2\pi v^2 \quad (11),$$

where v is as defined in chapter 1. A combination of the initial slope and one of the critical times, t_1 or t_2 , is sufficient to determine the position on the surface and completely define the simulated curve in the illustration for any type of units. To complete this example, illustration 22 shows three growth events resulting from three different initial positions.

For boundaries with a large number of edges, e.g. a square or irregular hexagon (both experimentally common)²¹, the number of critical encounters of the new layer with the boundary increases, increasing the number of critical points. Since the microscopic expansion rate is the velocity of the expanding layer across the surface, the critical times $t_1, t_2, t_3, \dots, t_n$ can be related to distances. These correspond to the distance from the origin of the new layer to the surrounding edges of the boundary. In the case of a circular boundary, the second critical time is redundant; however, this is not the case when the boundary is rectangular or elliptical.

A useful feature of critical point analysis is the possibility for computerized automation. Although visual assessment is the most efficient method for correlating the observed growth events to a surface geometry, computer driven analysis can quickly process a long time

series of data. An experimental time series of slow growth on silver single crystals consists of regions of zero current and current fluctuations resulting from nucleation and growth of two-dimensional layers. A critical point analysis program could skip through regions of zero current and find growth events by a level-crossing test. Once the growth event is found, least squares fitting of the early values generates the initial slope and the time position of the origin. Sharp deviations or discontinuities can be correlated to the critical points. Finally, the tail of the transient can be fit to determine the final critical point.

The details of modeling the growth of a circle into an ellipse and the computer-based analysis of these simulations have been studied here. Simulations were written and run in the ASYST scientific programming environment (Macmillan Software). The simulations utilized both the array math and graphics capabilities of this programming environment. Simulations were run on an AT&T 6300 plus IBM compatible computer. The computer used an 80286 CPU at 12 MHz and an 80287 math coprocessing chip. Three basic algorithms were investigated in the modeling of growth in this system. Criteria for a successful model were the ability to generate accurate reaction rate vs. time curves and a short total run time. Once a model was selected, several hundred growth events were calculated under different boundary conditions. The analysis techniques were developed on these data sets. The source code used for simulating growth events and the code for the analysis routines are included here in appendix C.

The first simulation algorithm attempted to describe the surface as a square grid of points. Each site on the surface was assigned a non-zero value if it was populated by the new layer. The difference in the sum over the grid at t_i and the sum over the grid at t_{i+1} gave the "charge" passed in the time step. A circular or elliptical mask could be used over the grid to provide the appropriate boundary conditions. These simulations were hampered by speed and memory considerations. These restrictions fixed the grid sizes at 100 by 100 points or smaller. Typical simulation runs required five to fifteen minutes to complete for a single growth event. With this grid size, the interactions with the boundary produced a sawtooth shape on portions of the simulated reaction rate curves. This was caused by the inability of a coarse square grid to smoothly reproduce a circle. Real crystals within macroscopic boundaries do not show this effect because the atomic grid is three orders of magnitude smaller.

The second simulation algorithm used a shell of points at a radius r . The shell points were checked at each time step to verify the number within the boundary. Between each time step, r was increased. The points within the shell were angularly positioned at random before the start of the growth event. The reaction rate was a function of the radius r multiplied by the number of shell points within the boundary. Typically, 100 shell points were used and the results of ten runs were averaged together to produce a simulated growth event. A single run required three minutes. The ten run average was effective in removing sampling errors; however, a simulated growth event required thirty minutes of computer time.

Converting the shell technique from a set of randomly positioned points to an equally angularly spaced grid eliminated the need for averaging of the runs. With 360 points with 1° spacing, a growth event simulation required five to eight minutes. The radial resolution in these simulations produced data which was one tenth of the expected experimental resolution. This resolution was estimated by the precision of our current measurement and the temporal spacing between experimental data points. Each grid point in the simulations corresponds to a surface area containing 10^5 atoms. A pair of simulated growth events created by this algorithm is shown in illustration 23. These two simulations show the difference in growth event shape when the initial cluster position is along the major and minor axes of an elliptical boundary. Typically, growth event initial positions were chosen at random by the computer. Series of transients for a set surface boundary were calculated in blocks of 100 and saved as binary files.

In order for a computer to perform critical point conversion to locations, the boundary must be determined. For an elliptical boundary, the length of one axis and the eccentricity are sufficient to describe the boundary. One of these factors, the minor axis length, is always known. When the surface normal is aligned along the capillary, the boundary is a circle with a diameter equal to that of the capillary. As the surface normal rotates off the direction of the capillary bore, the intersection of the plane of the surface with the capillary gives an ellipse, and the minor axis is the capillary diameter. To determine the eccentricity of this ellipse, the relative length difference between the

major and minor axis can be used. This is obtained from the experimental data by constructing what we call a rainbow plot.

These rainbow plots are constructed from the sums of the critical times extracted from the growth events. Illustration 24 shows a rainbow plot for a set of 100 growth events which originated at random surface positions. The spread in growth times is a result of the different distances over which the new layer expands. The number of events which occur for a particular $t_1 + t_2$ takes on the shape of an arc for a theoretically perfect distribution. This "total" growth time is a crude measure of the angular position. The events which take the longest to complete started at small angular deviations from the major axis. The events which have the shortest time to completion began near the minor axis. Along these two axes, multiplying the expansion velocity by the time t_1 gives the distance from the nucleation site to the nearest wall, and multiplying the expansion velocity by the time t_2 gives the distance to the farthest wall. By adding these two times together, a value which is proportional to the distance of the axis is obtained. This is true for all radial positions. The endpoints of the rainbow plots determine the relative difference between the major and minor axes lengths.

There were three steps then, in the conversion of a simulated or experimental data set into an original position. First, a computer routine scanned over a large number of growth events, extracting the critical times. Second, these critical times were used to determine the relative difference in length between the major and minor axes, providing an approximate boundary shape. Third, a computer algorithm

used the critical times for a particular growth event and the determined boundary to calculate the nucleation site for that growth event.

The computer analysis program used to analyze the simulations did not have to construct linear fits to the start of the events because the starting point of each event was the first point in the run. The time t_1 relative to the starting point was determined by looking for the first deviation from linear behavior. Once this first point had been determined, the computer scanned the data set until the simulation data dropped below a pre-set value. The previous five data points were fit by least-squares linear regression. From the regression coefficients, the intercept signaling the end of the growth event was determined. This gave the critical time t_2 .

The special significance of the critical times as discussed earlier is that they define the radius of the expanding layer when important interactions with the boundary occur. The first critical time, t_1 , is the time of first interaction of the cluster with the boundary. The cluster radius at this time, $r(t_1) = vt_1$, is the distance from the cluster origin to the nearest point on the boundary. Given t_1 and a boundary shape, a set of possible nucleation sites can be constructed; this is shown in illustration 25. At the second critical time, t_2 , the growing layer has reached the point on the boundary most distant from the nucleation site. The computer analysis algorithm used this second time to select the origin from the possible sites shown in illustration 25.

The position determination algorithm modeled the set of possible nucleation sites as shown in illustration 25 as an ellipse. The

eccentricity of the ellipse was determined by the possible sites along the major and minor axes of the original boundary. The second critical time was converted into a distance. The computer then searched for the interior normal to the boundary with this distance to the ellipse of possible nucleation sites. The normal to the ellipse approximates the farthest point from the nucleation site and is exactly correct along the major and minor axes. Previous algorithms for circle-into-circle position extraction used a line that passed through the center of the circle to describe the length $v \cdot (t_1 + t_2)$. This is rigorously correct because of the radial symmetry. For an elliptical boundary, this approximation was tried and it provided significantly poorer agreement when comparing the initial and calculated nucleation sites.

From our analysis of the simulated growth as described above, we concluded that the extraction of initial positions from experimental data is feasible. A small number, 50 to 100, of simulated growth events randomly distributed on the surface were found to allow accurate determination of the eccentricity of the boundary. This came as a surprise since it was expected that a large number of growth events would be required to sample the surface. The rainbow plots presented a distribution close to the theoretically expected distribution with a small number of runs. A set of 300 simulated events gave agreement to the known eccentricity within 1%. Since previous experimental work has been successful in capturing several hundred growth events over a short period, experimental determination of the surface boundary should be possible.

Converting the critical times extracted by the computer into coordinates by the algorithm developed was time efficient and accurate. Illustrations 26 and 27 show quadrants of a simulated surface at two eccentricities. The initial and calculated nucleation sites are shown for 25 simulated runs. The radial agreement of the calculated positions and the initial positions is very good. The angular agreement is not as good near the major and minor axes. Some of the deviations are due to the approximations in the position extraction algorithm. The assumption that the set of possible initial locations can be described as a second ellipse fails for long t_1 . This approximation seems to have the strongest impact on determining positions near the major and minor axes. Near the boundary, the angular coordinates are affected by the precision used in determining the intersection of the surface normal with the set of possible positions.

Higher precision in the calculations is possible for computer generated data sets. However, the precision used in determining the positions shown in illustrations 26 and 27 are consistent with presently available experimental resolutions. From these simulations of growth events we have drawn several conclusions.

Simple computer models can successfully simulate growth events for arbitrary and unusual boundaries. Models were able to determine curves with close to experimental resolution in short periods of time. This allows user-driven interactive fitting of data if required. The application of a scientific computing workstation would allow interactive simulation of data at the experimental resolutions. Computer based analysis of these events was successful due to the

distinctive nature of the critical points within the events. In the case studied here, numerical conversion from critical times to surface coordinates is fairly successful. We find that radial positioning is well-determined for the growth of circles into ellipses. The angular resolution is not as good, yet still good enough to reveal the approximate positions. Positional location within such a boundary opens the possibility for microscopic study of sites which are responsible for nucleation at the surface.

Modeling Experimental Data:

The shape of the growth event and the total charge passed in the growth events described in chapter 1 implied that a subset of the area within the capillary was the active surface. Several potential surface geometries and cluster shapes were explored in a manner similar to that of the previous section in order to find a sensible geometric model to describe the data. The model which was most consistent with the experimental data is shown in illustration 9 and reproduced with appropriate labels for this section in illustration 28a. The surface region which is active is a sector of a circle or ellipse. A computer program written to plot the data was modified to include a model calculation of the growth of a circular cluster on this active surface. The adjustable parameters in the model plot were selected by the user. The modeling program constrained the location of the initial cluster to the region at the capillary wall. The critical times used to generate the model were input by the user through picking points on the

experimental curves. The eccentricity of the region and the shift along the capillary towards the facet edge ($h - d$) were selected by the user and adjusted for the best fit with the experimental data.

Illustration 28a-d shows the basis for the model calculations and shows the various geometric regimes within the model. Since the geometry was restrictive, it was feasible to derive simple expressions for the current as a function of time. The form of the expression varied with the growth regime. The model program uses three regimes and calculates (numerically) the intersection points between the boundary and the growing layer. The growth current under this model is proportional to the radius of the cluster and the angular separation of the intersection points.

The first regime is shown in illustration 28b. Here, the cluster is unbounded on one side and is in contact with the edge of the crystal at the capillary wall. This period of the growth cycle is identical to the initial growth period shown in illustration 22 (curve c). Using the intersection points shown in illustration 28b, the current is given by:

$$i \propto r \cos^{-1} \left[1 - \frac{(x - x')^2 + (y - y')^2}{2 r^2} \right] \quad (12).$$

The intersection points x, y and x', y' are determined numerically for a particular r by finding the value:

$$x_e = \sqrt{A^2 \left(1 - \left(\frac{y}{B} \right)^2 \right)} \quad (13),$$

within ϵ of the value:

$$x_c = \frac{\left(\frac{r}{B}\right)^2 - \left(\frac{r}{A}\right)^2 + 2(x_0 - y_0) + 2y(1 - \left(\frac{r}{B}\right)^2)}{2(1 - \left(\frac{r}{B}\right)^2)}$$

(14).

The deviation value typically used was $\epsilon = 0.001 \mu\text{m}$; in the two expressions above, x_e is from the shape of the elliptical boundary and x_c results from the intersection of a circle of radius r located at x_0, y_0 with that boundary. As r increases, the two solutions to these equations, x, y and x', y' , move away from the growth origin.

The second regime is shown in illustration 28c. In this period of the growth cycle, there are four intersection points of the critical cluster with a boundary: x, y ; x', y' ; x'', y'' ; and x''', y''' . The first two are given by equations 13 and 14, as in the first regime. The other two intersection points result from interaction with the facet edge and they are given by:

$$x'' = x''' = A - h \quad (15),$$

$$y'' = y_0 + \sqrt{r^2 - (x'' - x_0)^2} \quad (16),$$

$$y''' = y_0 - \sqrt{r^2 - (x''' - x_0)^2} \quad (17).$$

The current is given by:

$$i \propto r \left[\cos^{-1} \left[1 - \frac{(x - x')^2 + (y - y')^2}{2r^2} \right] - 2\cos^{-1} \left[\frac{x'' - x_0}{r} \right] \right] \quad (18).$$

The third regime is shown in illustration 28d. At this point, the new layer has expanded over most of the surface and has completely stopped growing on one side. The current resulting from filling the remaining portion of the substrate is given by:

$$i \propto r \cos^{-1} \left[1 - \frac{(x' - x''')^2 + (y' - y''')^2}{2 r^2} \right] \quad (19),$$

where x', y' and x''', y''' are as defined above; this result is analogous to equation 12.

The modeling program calculated the expected current for a hypothetical cluster as a time series starting at the user input origin. The program increased the size of the cluster in each experimental time step by the distance indicated by the initial slope of the experimental data. The radius of the cluster at each time step was compared to the geometry to determine the relevant growth regime. The appropriate equation above was then used to determine the model instantaneous current. For the simulations of growth events occurring on these approximately 10 μm wide crystal facets, the total time to generate 300 model points was approximately 4 minutes.

The model for the surface and growing cluster used in this section was selected on the basis of its match to known geometric constraints and its flexibility. Some example output from this modeling routine is provided in illustrations 29 and 30. The variation in basic form as the eccentricity increases is shown in illustration 29. These model curves are displayed in arbitrary time units to emphasize the changes in the

position of the peak of the transient with respect to the start and end time. As the eccentricity increases, the first regime growth signal deviates from linear behavior. Comparing models of growth events of equivalent charge, it was found that the first critical time, the time to the peak of the event, increased with increasing eccentricity. A change in eccentricity is indicative of change in the tilt of the active surface. For all series which we observed, the eccentricities were self-consistent from growth event to growth event. However, analysis of individual series corresponding to different active surfaces revealed a range of experimental eccentricities. This is best explained by the presence of multiple crystal facets, with different angular orientations (c.f. illustration 17a).

Illustration 30 shows the effect of moving the nucleation site along the edge of the capillary. For simplicity in the model, the shift in position is represented as distance shifts with respect to the microfacet size h . Angular position is determined by solving for position using the known boundary geometry. Shifts in the initial position of the cluster toward the facet edge cause longer total growth times and make the extent of the final growth regime longer.

Illustration 15 from chapter 1 shows an experimental growth event and a model curve. The total charge under the model curve is equal to the growth event charge. The model curve was generated at an eccentricity of 0, meaning that this active surface had a normal close to the direction of the capillary bore. By adjusting the position of the initial cluster, the final portion of the growth event is properly fit. Typically, a range of distance shifts ($h - d$) produced equally

good fits. The range of values was around 30% of the total distance shift. Although the experiment and model do not show an exact point-to-point correlation, the experimental and model curves show the same number of growth regimes, in approximately the same places. The quality of the fits between the experiments and model is better in this work than in work reported elsewhere^{26,27,29}, this is due to the flexibility and appropriateness of the geometric model.

The range in distance shifts of the initial cluster generates two rather wide portions of possible nucleation site locations. Illustration 31 shows this shortcoming. For the set of events shown in illustration 18, the average shift is 630 nm and the range is ± 100 nm. This creates a region along the boundary about 1 μm in length of possible positions. The actual active site is probably not that large, our data quality simply prevents interpretation with better resolution. Based on the deterministic nature of the observations, we have been able to conclude that a single portion of the surface was active; however, we are not able to count the number of sites within this region.

The quality of the fit obtained to the experimental data by a model which treats the new layer as a circular entity is intriguing. Under these conditions, the new layer seems to be growing under kinetic control. Thermodynamic control would produce small polygons on the surface. The polygons should provide significantly different critical behavior than what is observed. Within our experimental resolution, kinetically limited growth with a single isotropic expansion rate is the best explanation of the observed growth behavior. Near the maximum current in the data, there is a deviation from the model curve. This

deviation may be signalling the failure of the circular cluster model or may reflect a deviation from a straight line at the facet boundary.

This is the major shortcoming of this modeling technique; in the end, there are basic assumptions which must go into the model before interpretations can be made. However, the strength of the growth and surface event analyses presented in the previous two sections is that they can quickly provide information about active surface sites and kinetic parameters. Future work may be able to use these analysis techniques as the starting point for probes which have finer resolution but are unsuitable for application to realistic surfaces because of their size.

Modeling Surface Diffusion:

The surface motion of absorbed species plays an important role in many aspects of chemistry and physics at surfaces and interfaces. The behavior of our observed regular growth events as discussed in chapter 1 appears to be another example. Species transport by diffusion is a topic which has been well developed. Previous analytical and computational treatments of surface self-diffusion have investigated concentration effects and adsorbate interactions⁵³⁻⁵⁵. The most common description of atomic or molecular diffusion is based on a random walk. In this random walk, the particle's trajectory is determined by motion from site-to-site. The probability of hopping from one site to another is independent of the direction of the hop and no memory of the previous hop direction is maintained. Solution of Fick's Second Law under the

appropriate boundary conditions for a free standing particle(s) leads to:

$$\langle r^2 \rangle = 2dDt \quad (20),$$

where d is the dimensionality of the system, $\langle r^2 \rangle$ is the mean squared displacement of the particle(s) at time t and D is the diffusion coefficient. The mean squared displacement is used as a descriptive quantity because the hop statistics constrain the mean displacement to zero.

This functional form is consistent with our observations; however, it does not provide the correct conversion from the slope of the size vs. square-root of waiting time fits to the diffusion coefficient. In the experiment, the boundary conditions are consistent with diffusion from an area of equilibrium concentration across a depleted region. The capillary wall produces a boundary which prevents motion in one direction beyond a certain point. The experiment does make a clear and simple measurement of the transport between these two boundaries. However, since one boundary is slightly elliptical, derivation of a simple two-dimensional analytical result proved quite difficult.

The regular growth events provide the data from pseudo-one-dimensional diffusion experiments. The equilibrium region acts as source. The nucleation site at the capillary wall creates a growing cluster which is detected by the steady-state current measurement. The time from a growing layer's contact with the facet edge to the start of

the next event determines the time required for surface species to diffuse from the source to the nucleation site.

The waiting time between growth events of similar total charge (hence, similar facet size) varied slightly. Variations in the waiting time can be caused by the nucleation process or by a spread in surface species arrival times. To determine the magnitude of these variations and their implications for the nucleation process, groups of events of the same facet size were compared. The waiting time was divided into two parts; the minimum time required for surface species arrival, and a variable cluster arrival time. The typical variable arrival time was about 10% of the minimum waiting time. As stated earlier, the cluster arrival time technically reflects both the time variance of the nucleation process and surface diffusion. The variable cluster arrival time can be used to place an upper bound on the critical cluster size in the nucleation process. The variance of the variable cluster arrival time is equal to the nucleation rate, under the assumption that the nucleation process can be described as a Poisson process.

The upper bound to the nucleation rate indicated that very small critical clusters were involved in the nucleation process. In fact, an atomistic treatment of the nucleation process might be more appropriate to determine the actual critical size because the balance of energies nucleation equation predicts a critical cluster with less than 5 atoms. Regardless, the upper bound in critical cluster size is very small, implying that the diffusion process need only provide a few surface species before the critical cluster forms and growth begins. We have tried computational simulation as an approach for studying the effects

of random surface species motion with respect to this problem. The simulations studied the arrival times of hypothetical diffusing species moving in a random walk. By conducting actual simulations, it was possible to select the arrival times for the first, second, third, etc. surface species. In the simulations, the hopping probability and the diffusion length were varied in order to study the spread in arrival times resulting from the diffusion process.

For surface diffusion of a small number or even a single species to be a viable explanation of the experimental observations, it needed to be shown that a random walk model produced a low spread in arrival times under the appropriate conditions. Our experimental results which measured the surface transport of a species demonstrated only a 10% variation in the arrival time. In the limit of a small number of hopping species diffusing over a short region, it is intuitive that the arrival time could fluctuate significantly. By modeling large systems, the effects on the arrival time statistics could be studied when the number of hop attempts moved into the area of 10^6 to 10^7 .

The diffusional process was modeled by a random walk by applying a computer Monte Carlo method to each surface species. This method was chosen due to its ability to treat very large systems quickly. The total probability of movement in a time step was varied from 0.8 to 0.002. The lower value represents the typical hop success based on the activation barrier to diffusion for fcc(111) silver as determined by molecular dynamics calculations^{39,40}

Both two-dimensional and one-dimensional simulations of the surface were conducted. The results from the two-dimensional study will

not be reported here. This is because the small number of surface sites required to make these calculations temporally accessible produced arrival times with a very large spread. The one-dimensional simulations provide a reasonable approximation to the problem since the diffusion region is a short line across the wide strip of the active facet, see illustration 32.

A computer program was written in FORTRAN to run sets of simulations. The simulations were run on IBM compatible personal computers with 80286 and 80386 central processors. Typical simulation times ranged from a few minutes up to a few hours. The program could be adjusted to allow verification of the simulation technique by equation 20. The simulation code is quite short and is included here:

```
C THIS IS THE SOURCE CODE FOR TORSD5.FOR, A COMPLETE AND
C WORKING SIMULATION PROGRAM. MICROSOFT FORTRAN 4.1
C TIM ROBINSON    LAST REV 12/15/89
```

```
BLOCK DATA DIFFUSION
COMMON /INFO/ ISURF(5000), BHOP, FHOP, IFAP, IEQ, ISEQ
INTEGER*1 ISURF
INTEGER IFAP, IEQ, ISEQ
REAL BHOP, FHOP
DATA IFAP /1/, IEQ /3/, BHOP /0.200/, FHOP /0.100/
DATA ISURF /5000*0/, ISEQ /40/
END
```

```
C HERE'S AN EFFECTIVE PORTABLE RANDOM NUMBER GENERATOR:
C FROM "NUMERICAL RECIPES", W. H. PRESS ET.AL., CAMBRIDGE
C UNIVERSITY PRESS, 1986, P. 195. NEGATIVE IDUM RESETS (See Ref. 56)
```

```
REAL FUNCTION RAN1 (IDUM)
PARAMETER (M=714025, IA=1366, IC=150889, RM=1. / M)
INTEGER*4 IRADUM, IDUM
IF (IDUM .GT. 0) IRADUM = IDUM
IRADUM=MOD(IRADUM*IA+IC,M)
RAN1=IRADUM*RM
END
```

```
C INITIALIZATION SUBROUTINE
SUBROUTINE INITIAL
```



```

COMMON /INFO/ ISURF(5000), BHOP, FHOP, IFAP, IEQ, ISEQ
INTEGER*1 ISURF
WRITE(*,*) 'INPUT HOPPERS, EQ. BOX SIZE, HOP PROB.'
READ(*,*) IEQ, ISEQ, PRHOP
BHOP = PRHOP
FHOP = BHOP / 2.
END

```

C SIMULATION ARRAY INITIALIZATION SUBROUTINE

```

SUBROUTINE SETUP
COMMON /INFO/ ISURF(5000), BHOP, FHOP, IFAP, IEQ, ISEQ
INTEGER*1 ISURF
DATA ID /-1/
DO 10 I = 1,IEQ
L = INT(RAN1(ID)* ISEQ) + 1
IFAP = MAX(L, IFAP)
10 ISURF(L) = 1
END

```

C HOPPING SUBROUTINE FOR FIRSTBOX

```

SUBROUTINE FIRSTHOP
COMMON /INFO/ ISURF(5000), BHOP, FHOP, IFAP, IEQ, ISEQ
INTEGER*1 ISURF
DATA ID /-1/
IMET = ISURF(1)
DO 10 I = 1,IMET
IF(RAN1(ID) .LT. FHOP) THEN
ISURF(1) = ISURF(1) - 1
ISURF(2) = ISURF(2) + 1
END IF
10 CONTINUE
END

```

C EQUILIBRIUM SUBROUTINE

```

SUBROUTINE EQUILIBRIUM
COMMON /INFO/ ISURF(5000), BHOP, FHOP, IFAP, IEQ, ISEQ
INTEGER*1 ISURF
DATA ID /-1/

```

C COUNT HOPPERS IN EQUILIBRIUM REGION

```

ISUM = 0
DO 10 I = 1,ISEQ
10 ISUM = ISUM + ISURF(I)
IDIFF = IEQ - ISUM

```

C ADD OR SUBTRACT HOPPERS TO HEAD TOWARDS THE EQUILIBRIUM VALUE

```

IF (IDIFF .EQ. 0) THEN
IF (ISURF(1) .GT. 0) CALL FIRSTHOP
ELSEIF (IDIFF .EQ. 1) THEN

```

```

      IF (ISURF(1) .GT. 0) CALL FIRSTHOP
      IF (RAN1(ID) .LT. 0.2) ISURF(1) = ISURF(1) + 1
    ELSEIF (IDIFF .EQ. 2) THEN
      IF (ISURF(1) .GT. 0) CALL FIRSTHOP
      IF (RAN1(ID) .LT. 0.4) ISURF(1) = ISURF(1) + 1
    ELSEIF (IDIFF .GT. 3) THEN
      IF (ISURF(1) .GT. 0) CALL FIRSTHOP
      ISURF(1) = ISURF(1) + 1
    ELSEIF (IDIFF .LT. 0) THEN
      IF ((ISURF(1) .GT. 0) .AND. (RAN1(ID) .LT. 0.8)) THEN
        ISURF(1) = ISURF(1) - 1
      END IF
    END IF
  END IF
END

```

C MOVEMENT SUBROUTINE

```

SUBROUTINE MOVETHEM
COMMON /INFO/ ISURF(5000), BHOP, FHOP, IFAP, IEQ, ISEQ
INTEGER*1 ICHECK, ISURF
INTEGER IFRR
REAL RHOP
DATA ID /-1/
IFRR = IFAP
DO 100 I=IFRR,2,-1
  ICHECK = ISURF(I)
  IF (ICHECK .GT. 0) THEN
    DO 50 J=1,ICHECK
      RHOP = RAN1(ID)

      IF (RHOP .LT. FHOP) THEN
        ISURF(I) = ISURF(I) - 1
        ISURF(I+1) = ISURF(I+1) + 1
        IFAP = MAX(I+1, IFAP)
      ELSEIF (RHOP .LT. BHOP) THEN
        ISURF(I) = ISURF(I) - 1
        ISURF(I-1) = ISURF(I-1) + 1
      END IF
    END IF
  50 CONTINUE
  END IF
100 CONTINUE
END

```

C MAIN BLOCK OF THE PROGRAM

```

PROGRAM TORS1
COMMON /INFO/ ISURF(5000), BHOP, FHOP, IFAP, IEQ, ISEQ
INTEGER*1 ISURF
INTEGER*4 ICNT /0/, IRES(50)
INTEGER ISNUM, IBRDR
DOUBLE PRECISION XSUM /0./, XSQDIF /0./, BEAN, STDEV
WRITE(*,*) 'INPUT POSITIVE SEED'
READ(*,*) ID

```

```

X=RAN1(ID)
WRITE(*,*) 'INPUT "9" TO CHANGE DEFAULTS'
READ(*,*) IANS
IF (IANS.EQ. 9) CALL INITIAL
WRITE(*,*) 'NUMBER OF SIMULATIONS (<=50)'
READ(*,*) ISNUM
WRITE(*,*) 'LOCATION OF BORDER'
READ(*,*) IBRDR
IBRDR = IBRDR + ISEQ

C MAIN SIMULATION BLOCK

      DO 100 I = 1, ISNUM
      CALL SETUP
20    CALL EQUILIBRIUM
      CALL MOVETHEM
      ICNT = ICNT + 1
      IF (IFAP.LT. IBRDR) GOTO 20
      WRITE(*,*) ICNT
      IRES(I) = ICNT
      IFAP = 1
      ICNT = 0
      DO 90 J = 1,5000
90    ISURF(J) = 0
100   CONTINUE
C COMPUTE STATISTICS ON RESULT
      DO 200 I = 1, ISNUM
      XSUM = XSUM + FLOAT(IRES(I))
200   CONTINUE
      MEAN = XSUM / FLOAT(ISNUM)
      DO 250 I =1, ISNUM
250   XSQDIF = XSQDIF + (IRES(I) - BEAN) ** 2.
      STDEV = DSQRT(XSQDIF/(ISNUM-1))
      WRITE (*,300) MEAN,STDEV
300   FORMAT (' MEAN = ',F10.2,' ONE SIGMA = ',F10.2,)
      END

```

The one-dimensional surface region is modeled as an array of byte values (array ISURF), see illustration 32. The value contained in each array element is the number of surface species at that site. An adjustable size equilibrium region is located at one end. One subroutine in the program checks the population within this region at the start of each time step. The population is adjusted by introducing more surface species or removing them at the edge of the equilibrium

box. All surface species were given equal probability of hopping to the left or right as in illustration 32.

The simulation code stops the run when the farthest reach of one of the atoms strikes the border region. Until then, the movement routine starts at the outlying region and works toward the equilibrium region, conducting hop attempts for all species at a surface site. In developing simulation code, the effects of three sampling methods were studied. The first simulation programs allowed a maximum of only one hop per surface species per time step. The overhead required to account for each surface species, individually, significantly slowed execution. The other two algorithms either scanned from the equilibrium region, making hop attempts for all species at a site, or scanned towards the equilibrium region as the code here does.

The problem encountered with the latter techniques was the occasional observation of double hops in a time step. At low hop probabilities, the chance of a double hop was reduced. At total hop probabilities of 0.2 or less, these latter two algorithms with the same input seeds produced arrival times within 10% of each other. After the majority of the simulations were completed, an additional algorithm was considered. It retains most of the processing speed of the code shown here and eliminates the sampling errors.

Instead of maintaining one array of values holding the contents of the surface sites, two arrays are used. On all the odd numbered time steps, the first array is used as the number of surface species at a site. The species after successful or unsuccessful hop attempts are placed in the appropriate location in the second array. On the even

numbered time steps, the second array is used as the source for site contents and the results of the hop attempts get placed back in the first array. Between the time steps, the target array is cleared so that simple summing at sites produces the correct number of species at each site. This approach would lend itself well to massively parallel computing systems. In the near future, it should be reasonable to simulate this type of problem with atomic resolution.

Our simulations used a range of diffusion lengths (l). Site numbers ranged from 50 to 1,000 from starting point to detection site. The actual number of surface sites over a 10 μm strip of a silver close-packed plane is around 50,000. The results of simulation runs for the various diffusion lengths were expressed as a ratio;

$$\beta = \frac{D}{D_{\text{obs}}} \quad (21),$$

where D_{obs} is the diffusion coefficient observed from the simulation and D is the diffusion coefficient expected in the lack of a concentration gradient. The resulting β values were plotted as a function of $1/l$. These plots showed a linear behavior over the values studied. Extending the results to zero $1/l$ provides a numerical estimate of β for the experimental data.

Simulations revealed that β was a function of hopping probability, concentration within the equilibrium region and, as mentioned above, the diffusion length. These conclusions are consistent with accepted models of diffusion under similar conditions. A set of simulations for a given l at various hopping probability were extended linearly to get the β

value used in the $1/l$ plots. Table 4 summarizes values for β for a range of hopping probabilities and diffusion lengths, using the equilibrium concentration of surface species as determined by a.c. impedance spectroscopy in chapter 1. Illustration 33 shows the results extended to zero hopping probability and plotted vs. $1/l$.

length	β at Hopping Probability:					low Pr. limit
	0.4	0.3	0.2	0.1	0.05	
50	0.851	0.912	1.002	1.022		1.098
75	0.626	0.668	0.774	0.834	0.856	0.897
100	0.496	0.555	0.593	0.633		0.681
200	0.330	0.368	0.411	0.380		0.412
500	0.225			.250		
1000			0.218			

Table 4. Simulation results for several diffusion region lengths and hopping probabilities. The right-most column contains the extrapolations to the low hopping probability limit used in illustration 33.

The spread in arrival times for the first surface species fell with decreasing hop probability and with increasing diffusion length. For a hop probability of 0.2 and diffusion lengths of 50, the standard deviation in arrival times for 30 runs was on the order of the average arrival time. For a diffusion length of 200 hops the standard deviation was half of the mean arrival time. The normalized deviation decreased linearly with the square-root of the diffusion length. This projects a standard deviation of 3% in the arrival times for the number of hops required in the experiment. The difference in arrival time between the

first and the first few surface species became very small when linearly extended to the experimental diffusion length. In all, the simulations supported the model proposed in analysis of the experimental data, in both of these areas. It appears that a system of randomly hopping species can demonstrate a low deviation in arrival times and supply a small number of surface precursors to the nucleation process.

Our simulations provide the means for converting the observed constant D_{obs} from the experimental data,

$$\langle h^2 \rangle = 2D_{\text{obs}}t + (h - d)^2 \quad (22),$$

to the traditionally reported surface diffusion coefficient D_s . The second term in expression 22 accounts for shifts of the nucleation site along the capillary which make the nucleation site closer to the facet edge. For the equilibrium surface concentration at $T = 20^\circ\text{C}$, we calculate $\beta = 0.19 \pm 0.02$ and for $T = 50^\circ\text{C}$, we calculate $\beta = 0.20 \pm 0.02$. The error bars reflect uncertainty in the fits of the β vs. $1/l$ plots and the systematic errors resulting from the simulation algorithms. Using these coefficients, experimental results as shown in illustration 19 are converted to the diffusion coefficients in Table 3, chapter 1.

Summary:

This chapter has presented results of computational modeling of growing surface systems. It was shown that computer modeling of the

growth of a circular layer onto an elliptical substrate is feasible, and the results of these simulations were used to develop positional analysis routines. Most importantly, these positional analysis routines were largely successful in determining the nucleation site of a growth event given the time dependence of the growth reaction rate. Experimentally observed growth events were modeled in the same manner. Finally, one-dimensional hopping simulations were used to verify assumptions in the analysis of regular growth events and provide corrections to observed diffusion coefficients.

illustration 20: Examples of symmetry-equivalent sites resulting from critical point analysis. For the rectangular surface, all events are mapped into one quadrant even though they could have originated in any of the four quadrants. Only radial information is accessible for events on a circular surface.

Critical Points in a Growth Event

illustration 21: Time-dependent current signal of a growing two-dimensional layer. The inset figures show the boundary and the new layer (dark hatching) at the three critical points in the time series. For this calculated event, the growing cluster was initially placed at a radial position half-way between the center of the circle and the boundary.

Three Simulated Growth Events With Different Nucleation Sites

illustration 22: Three simulated growth events showing the variation in the time dependent current. Curve b is from the same position as in the previous illustration. All three growth events are plotted on the same current scale and the charges under all curve are identical. For growth events starting at the boundary edge, the initial slope is exactly half of the other growth events.

Two Growth Events Within An Elliptical Boundary

illustration 23: Growth events simulated on an elliptical boundary. The initial positions are equal distance from the centroid of the ellipse. The curves are identical until the layer has the first interaction with the capillary boundary. Curve a results from an initial position along the major axis. This curve reaches a higher maximum and ends after curve b.

illustration 24: Histogram of summed growth time $t_1 + t_2$ for 100 growth events and an approximate model curve. The summed times (squares) are placed in 16 equally spaced bins for clarity. The heavy solid line is an approximate curve derived under the assumption that the line from the initial site to the final critical point passes through the origin. The left-most bin, smallest $t_1 + t_2$, is from events which are close to the minor axis. The width of the "rainbow" with respect to the magnitude of $t_1 + t_2$ reveals the eccentricity of the boundary.

illustration 25: Representation of the intermediate construction used in conversion of critical times into positions. The first critical time multiplied by the expansion rate generates a strip of potential initial sites. The distance which results from the second critical time determines the nucleation site from the set of potential sites.

Initial and Calculated Positions $e=0.35$

illustration 26: Comparison of initial positions for simulations and calculated positions based on the growth events. A set of 25 positions selected at random on the surface is shown here. The mean displacement between initial and calculated position is 800 nm for a capillary diameter of 76.2 μm .

Initial and Calculated Positions $e=0.65$

illustration 27: Comparison of initial positions for simulations and calculated positions based on the growth events. A set of 25 positions selected at random on the surface is shown here. The mean displacement between initial and calculated positions is 540 nm for a capillary diameter of 76.2 μm .

illustration 28: Sketch of elliptical boundary, active surface area, and the three growth regimes in this system. The active sector shape is shown in a with total sector width h , and distance from facet edge to nucleation site d . The coordinate axes; major axis A , and minor axis B , are shown for reference. The layer in the first growth regime has two boundary intersections and is shown in b. This regime holds until the radius of the new circular layer, r , is equal to or greater than d . At this point, growth regime 2 is entered c, followed by growth regime 3, d. The third growth regime is eliminated when $d = h$.

Model Curves for Different Eccentricities

illustration 29: Four simulated events originating on a boundary with varying eccentricity. The events are for surface regions with eccentricity; 0.0, 0.3, 0.6, and 0.9. The event on the circular boundary peaks first, followed by the event on a $e = 0.3$ boundary and the others with the latest peak from the $e = 0.9$ boundary. These curves are plotted on arbitrary charge scales and time scales with respect to each other to emphasize the differences resulting from boundary eccentricity. The most notable difference is that the events on the more eccentric boundaries show a significant deviation from linearity. A secondary effect is the shift in the peak position with respect to the total growth time, this effect is exaggerated by the normalization conditions shown here.

Model Curves for Different Initial Positions

illustration 30: Four model curves for different values of $h - d$. The more an event is shifted toward the facet edge, the earlier the peak current is reached. For no shift, the transition into the third regime is not observed. The shifts plotted here bracket the approximate range in shapes observed over a number of experimental observations.

illustration 31: The impact of uncertainty in d on the position determination. For the experimental data, the shift $(h - d)$ was very small when compared to h . This makes errors in d map onto large portions of the circular or elliptical boundary.

illustration 32: Methodology of surface diffusion simulations. The surface is modeled as a narrow diffusion zone, and local periodic boundary conditions allow direct extension to a one-dimensional simulation. At left is a schematic of the array used for the simulation. The concentration in the equilibrium region is exaggerated for clarity. The probabilities of a hop to the left (Pr_l) and a hop to the right (Pr_r) were half of the total hop probability.

illustration 33: Results from a set of diffusion simulations. The equilibrium region for these simulations is from the $T = 20^{\circ}\text{C}$ results of the a.c. impedance studies. The best-fit linear regression line is shown; $r^2 = 0.986$.

CHAPTER 3

SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY OF REALISTIC SURFACES

Introduction:

The scanning tunneling microscope (STM) introduced by Binnig et al.⁵² in 1982 has led to an explosion in studies of local microscopic surface structure. The STM and a force-based analog, the atomic force microscope (AFM)⁵¹, allow study of surface physical and electronic structure on atomic length scales. The STM and AFM are actually quite flexible instruments with respect to surface feature resolution. Our use of a STM has focused on physical features less than a nanometer to several tens of nanometers in size. The STM allows study of physical and electronic defects that are present on realistic surfaces in a range of environments. Surface defects and their effect on local electronic and physical structure are the area of interest of this work. A special emphasis has been placed on developing techniques which can make independent, simultaneous measurements of the electronic and physical structure of surfaces on the nanometer length scale.

The basics of scanning tunneling microscopy will be discussed here. There are several reviews of this topic that can provide additional information⁵⁷⁻⁶². Historically, electron tunneling physics has been investigated through the use of solid state devices^{63,64}. The solid state devices attained a stable tunneling current through the use of large contact areas. The earliest stable solid state tunneling devices have been attributed to Esaki⁶⁵. These devices consisted of

narrow semiconductor pn junctions. This work spurred interest in the fabrication of devices of metal strips separated by a thin insulating layer, and semiconductor/metal tunneling devices. Fisher and Giaever⁶⁶ are credited for constructing the first stable metal/insulator/metal junction. Their work and the work of others used very low junction temperatures, on the order of a few degrees Kelvin.

Vacuum electron tunneling was first observed in field emission studies using sharp metal tips. A review of work in this area has been written by Good and Müller⁶⁷. It was not until the work by Binnig et al.⁵², however, that a stable scanning vacuum junction had been prepared. These junctions were observed to be stable over a range of temperatures, up to and exceeding room temperature. Scanning tunneling junctions were fabricated from a very sharp metal tip and a conducting substrate. Piezoelectric devices capable of precise positioning held the tip over the sample at distances on the order of nanometers. The sharp tip allowed positioning and tunneling over very small surface areas. This sharp tip is the key to the use of these junctions as devices capable of measuring the structure of microscopic surface features.

The STM bases its operation on the elastic tunneling of electrons. The basic one-dimensional electron tunneling problem applied to the STM has been treated theoretically by Tersoff and Hamann⁶⁸ under the Wentzel-Kramers-Brouilllin approximation by the Bardeen⁶⁹ tunneling formalism. When two surfaces with delocalized electronic states approach one another, the exponentially-decaying evanescent wavefunctions from each surface can overlap at short separations.

Although the local potential barrier between the two surfaces is on the order of 4-5 eV in vacuo, it is possible for electrons to tunnel through this classically forbidden region. Illustration 34 provides a pictorial representation of the electronic structure of the junction. Under these conditions, Tersoff and Hamann have shown that the tunneling current is:

$$i_t \propto V_s \cdot \rho_t(E_f) \cdot \rho_s(E_f + eV_s) \cdot \exp\left[-\frac{s \cdot \sqrt{8m\phi_{eff}}}{h}\right] \quad (23),$$

Where $\rho_t(E_f)$ is the density of tip states at the Fermi energy, $\rho_s(E_f + eV_s)$ is the density of sample states at the Fermi energy plus the sample bias and ϕ_{eff} is the effective tunneling barrier. Their derivation assumes a tip with spherical symmetry and low sample bias compared to the barrier height. A subsequent treatment by Chen⁷⁰ has extended their approach to a tip of parabolic symmetry, with qualitatively similar results.

Experimentally, scanning tunneling junctions are operable in two modes. In the first, the scanning tip is moved in space without regard to the presence of the sample. This is the "open-loop" mode. Typically, the tip is scanned roughly parallel to the plane of the surface over a small, square, surface region, that may be tens to a few hundred of angstroms on a side. The tunneling current fluctuates during the scan and is recorded as a function of tip(x,y) coordinate. The fluctuations in tunneling current can be correlated to electronic and physical surface structure through equation 23. This mode of operation is often called constant-height or fixed-height, a slight misnomer. In the second mode of operation, the tip position is controlled by an

active feedback loop designed to maintain a constant quantity of a measured signal. The most common input signal for the feedback circuitry is the current flowing through the junction. When the tip is scanned over the surface, the vertical deflections required to maintain the feedback parameter (e.g. the tunneling current) constant are recorded. These deflections can be roughly correlated to the surface topography. In the limit of constant surface composition and tunneling transmission factors, the apparent topography is directly related to the physical structure of the surface. This mode is often referred to as the constant-current or fixed-current mode. More generally, the feedback method can be described as the "closed-loop" mode.

Along with scanning probe experiments at a constant junction bias, recently low temperature "spectroscopic" techniques have also been applied by several researchers to these experiments performed at room temperature. Hamers⁶⁰ has published a review of recent work in scanning tunneling spectroscopy (STS). At room temperature, thermal energy has a significant impact on the electronic state occupancy of electrons close to the Fermi level. This broadens the energy resolution of tunneling experiments to roughly $\pm 2.5 kT$ ⁶³, (± 65 mV at room temperature), preventing the observation of low-energy inelastic vibrational transitions, for example. However, spectroscopic techniques have been successfully applied to study electronic band structure at the surfaces of semiconductors and metals. Spectroscopic information can be acquired in both one-dimensional and two-dimensional experiments. The small-signal conductance (di/dV) at constant bias is commonly used in STS following the work performed on solid-state devices^{60,63,64}.

The small-signal conductance is experimentally measured in one of two ways. One type of conductance measurement attempts to hold the tip and sample at fixed-height while the bias is linearly ramped over the range of several eV. The measured $i(V)$ curve is differentiated with respect to bias to yield the conductance as a function of bias. The conductance can also be measured directly with lock-in amplifier techniques under conditions of constant separation and d.c. current. The first type of measurement is faster than the second type of measurement; however, there are two significant problems with the technique. The bias ramp can be damaging to the physical state of the tunneling junction. Recent work has demonstrated the power of the tip to cause surface modification⁷¹. These modifications are triggered by high bias or fast voltage sweeps, and until the mechanism is understood fully, the possibility that the tip is modifying the surface during the acquisition of the $i(V)$ curve cannot be eliminated. The $i(V)$ curve method also sacrifices dynamic range at low bias and current, because of the extremely small currents passing between tip and sample at low bias.

The form of (di/dV) as a function of bias is dependent on several junction parameters. In practice, the small-signal conductance is normalized by the d.c. conductance to reduce contributions from bias-dependent tunneling transmission terms related to changing the effective barrier under the conditions of the experiment⁷². Lang⁷³ has demonstrated that $(di/dV) \cdot V/i$ is roughly proportional to the density of states in certain systems. The true functional form is probably closer to that given by Hamers (ref. 60 page 542):

$$\frac{d[\ln(i)]}{d[\ln(V)]} = \frac{\rho_S(E_f + eV_S) \cdot \rho_t(E_f) + A(V_S)}{B(V_S)} \quad (24),$$

where $A(V_S)$ is related to the integral over energy of the derivative of the junction transmission terms with respect to bias and $B(V_S)$ is the integral over energy of the transmission terms. Starting with the result from Tersoff and Hamann (equation 23 here) it can be shown under our experimental conditions that the effective barrier and the tunneling area of the junction play a major role in the ratio $A(V_S)/B(V_S)$.

The STM has been very successful in elucidating for the first time the atomic structure of many surfaces^{57,58}. Moving beyond the determination of atomic scale corrugations to the study of electronic properties, or larger structural features, or adsorbed molecular species has been complicated due to ambiguity in interpretation of STM images. The theoretical treatments summarized above are valid only for physically and electronically simple systems and under very low applied bias. Study of many realistic surfaces in air has revealed that most surfaces retain a morphology that is dominated by bumps and hillocks^{61,62,74}. It is difficult to determine where the substrate surface ends and contaminants or intentionally deposited species begin. At this point in the development of the subject, a better understanding of how the microscope actually operates and the application of additional complementary techniques are both required in order to make progress in the development of the STM as a chemically surface-sensitive tool.

Our research has focused on developing instrumentation that is optimized for acquiring simultaneous images of topographic and

spectroscopic information. Once the raw experimental data has been obtained, it must then be analyzed quantitatively in a number of ways and visualized in an insightful manner, so these computational techniques have been developed as well in this research program. Our experimental apparatus measures the spectroscopic information at a single bias while scanning over the surface. One advantage of this approach is that numerical differentiation of an often noisy signal is avoided. Another advantage is that the tunneling junction is not exposed to the high voltage-sweep rates required to obtain current-voltage curves "on the fly". A significant experimental disadvantage of our approach is that the time to acquire a true conductance spectrum over the surface is longer because an entire image needs to be acquired at each bias.

By combining simultaneous images of topographic and spectroscopic information, local changes in the small-signal conductance can be correlated with the apparent surface structure⁷⁵. This approach has allowed us to obtain additional insight into the electronic properties of platinum and graphite surfaces in air. In the present work, the length scales of interest are on the order of nanometers to tens of nanometers. For imaging in this window, a reusable type of tip was developed for use along with more traditional STM tips. The rest of this chapter covers the basics of the microscope constructed during the thesis research and experimental observations of evaporated gold films, polycrystalline platinum, and highly oriented pyrolytic graphite.

Experimental:

Apparatus and Instrumentation Overview:

The hardware for the scanning tunneling microscope consists of four basic parts: mechanical mounting and vibration isolation apparatus; piezoelectric scanning system; tip and sample mounts; and customized electronics for microscope control and data acquisition. The main mounting apparatus includes two layers of acoustic foam shielding and is suspended by elastic cords. Two piezoelectric devices, one composite scanning drive with three elements and one single-element drive, were employed. The tips were about 1.2 cm long with a mounting post at one end. Samples were about 5 mm x 5 mm in size. The electronics for the instrument contained three subsystems; scanning and experiment control, experiment monitoring circuitry, and data acquisition system. Most of these aspects were developed as part of the thesis work.

Mounting and Isolation Hardware:

Illustration 35 depicts the basic mounting system of the microscope. A plywood board (chosen for its lossy acoustic transmission properties) supported by a unistrut frame serves as the mounting plane for a small vibration-isolation table. The plywood board is suspended by elastic (bungee) cords from a unistrut framework hung from the ceiling. The mechanical resonant frequency of this base plane when the apparatus is fully installed is on the order of one Hertz. The resonant frequency of the vibration-isolation table (Newport model TS-23) is

between 20 Hz and 50 Hz depending on the pressure of gas in the table supports. The frequency mismatch between the plywood plane suspension system and the vibration isolation table effectively eliminates propagation of building vibrations to the experiment. This suspension design borrows from Hansma⁷⁶ and others. Acoustic isolation is provided in two ways: a plexiglass enclosure that reflects sound waves and waffled composite fiber foam mounted on the underside of the plywood board and on the inside of the plexiglass box. A second layer of acoustic isolation is provided around the microscope itself by a small plexiglass box with foam on its inside walls. Each acoustic isolation layer provided about 20 dB of attenuation of laboratory noise. The overall vibration and acoustic isolation outlined here reduced the effects of laboratory noise sources (in a laboratory on the second floor of a building) so that they yielded interference on the order of the electronic noise in the system.

Scan Elements and Configuration:

The piezoelectric elements used in this microscope were fabricated by Burleigh Instruments, Inc. A three element PZT Aligner/Translator model PZ-81 was used to generate the scans across the surface and to control the tip position in "closed-loop" experiments. A basic PZT Pusher model PZ-40 was employed for coarse positioning of the tip and sample. Both piezoelectric devices were constructed of "hard" piezoelectric ceramic, providing relatively small deflections and very linear, non-hysteretic, behavior. The roll-off frequency for small-signal response is at 5 kHz for both devices. These elements were

configured in two ways, parallel (illustration 36) and coaxial (illustration 37). The parallel configuration was used for most of the work discussed here. The coaxial configuration was developed to provide lower drift rates after microscope assembly and simplify sample handling.

The parallel configuration used two MACOR[®] ceramic slabs as mounts for the piezoelectric drive elements. MACOR[®] was chosen because of its near-zero coefficient of thermal expansion at room temperature and lossy acoustic properties. One 3" x 3" x 1/2" MACOR[®] slab held the scanning PZT in the center and was rigidly mounted to the top of the vibration isolation table. The coarse adjustment single element PZT was mounted in one corner of the slab. These components were mounted on the reference (fixed) slab to reduce motion caused by residual stresses in power cables. The second ceramic slab was positioned on this reference frame by 6 ball-bearing contacts. Coarse positioning was accomplished in the plane of the slab by three 80 threads-per-inch (tpi) screws. The gross separation between the tip and sample was changed by tilting the movable slab by lengthening the coarse adjust screw or the coarse adjust PZT. Tilting the slab produced a mechanical disadvantage of 3:1 with respect to the length of a 80 tpi screw and the extension of the coarse PZT.

The coaxial configuration used a single mount to hold the entire microscope assembly. The reference MACOR slab from the parallel configuration was used without modification. In the coaxial configuration, the coarse PZT is held within the scanning PZT. A brass fitting with a micrometer mount was screwed onto the threaded end of the

coarse PZT. The micrometer was in turn mounted on the back side of the scanning PZT with an aluminum mount. The vertical position of the coarse PZT within the scanning PZT could be adjusted with the micrometer. The sample in this configuration is held in a ceramic fitting in a cap which screws onto the end of the scanning PZT. The miniaturization resulting from this design reduced translational drift rates by one order of magnitude.

Tip and Sample Mounting:

The tips and samples for the microscope were designed to work as plug-in parts in the parallel configuration. The tips were 1.2 cm in total length with a plug of about 0.4 cm of 18 gauge wire. The plug mated with a gold receptacle attached to the scanning PZT by a fiberglass mount plate. The samples were mounted on top of a gold receptacle identical to the tip mount. The mounting surface was circular with 0.10" diameter. By switching the basic mounting connector, samples on an 18 gauge post could also be used.

When the configuration was changed to the coaxial configuration, some mechanical changes were implemented in the tip and sample mounting. These changes eliminated the springy gold receptacles which may well have been contributing to start-up mechanical drift. Flat samples with thicknesses comparable to a glass microscope slide could be mounted to the MACOR holder within the sample cap. Samples of this type were held in place by a low contact pressure fit by a copper-beryllium spring. Thin metal samples could be used by placing a glass microscope slide of the same size on the back of the sample. Post-type (18 gauge) samples

and tips were held in place by a collar assembly. This provided a more rigid mounting point for both. Tips were mounted in the microscope by affixing the collar holding the tip to the end of the coarse PZT via a high-power magnet.

Electronics:

The scanning electronics were designed to take input deflections from an external source in the form of analog inputs in x, y, and z. The input signals were converted into drive signals which produced translation of the tip with respect to the sample. The scanning PZT consisted of three independent elements mounted to a 1" diameter drive ring. The elements were mounted at 120° separation. By proper scaling and combination of the input signals, the three elements could be used to achieve vertical translation (z) and horizontal translation (x and y). A symmetric application to all three drive elements produced the vertical translation. Two asymmetric combinations produced two orthogonal tilting modes in the plane of the tip mount. These tilts become deflections at the end of the 1.2 cm long tip. Illustration 38 shows the location of the individual piezoelectric elements, the symmetric drive mode, and one of the asymmetric modes. An analog computer was constructed from operational amplifiers to perform the conversion from input x, y, and z to the drive signals for elements 1, 2, and 3. High voltage operational amplifiers, Burr Brown 3582J, were used in the final stage to produce high-speed signals of up to 250 V. A schematic of the analog computer and high voltage drive circuitry is given in appendix D (figure D3).

Electronics to monitor the tunneling junction and control the position of the tip are also shown in appendix D. Current measurement was accomplished by a dual operational amplifier. Half of the amplifier converts the nA tunneling current into a mV signal while the other half drives a guard shield for the tip's electronic lead. A triaxial wire is used as described in chapter 1 for the current measurements. The monitoring circuitry produced a suitable signal for external acquisition and compared the tunneling current signal to a reference signal. The difference between these signals was converted into an applied deflection of the appropriate sign to the tip position. An integrating circuit of adjustable rise-time was used to reduce noise in the tip height control circuit.

Computer and Software Interface:

The final major electrical hardware component is the control computer and its hardware interface to the scanning and monitoring circuitry. The computer controlled the experiment by signals to the electronics of both analog and digital form. A Metrabyte DDA-06 board was used for these signals. The analog control signals from this interface board were used for x and y deflections and for the control signal to the coarse PZT. To prevent contamination of junction control signals by scan signals, a separate Metrabyte DAC-02 interface board provided the analog signals for fixed-current level and junction bias. Signals from the experiment in analog form were acquired by a Metrabyte DAS-50 analog-to-digital conversion board. An IBM-compatible DELL model

310, with 80386 CPU, 80387 math coprocessor and 8 Mb of RAM, was used for the experiments.

The software to run the experiment was written as part of the research project. Software for a STM must address several issues and also be capable of handling the large data sets which result from acquiring the image. Several computer programs were written to accomplish the tasks of acquiring and analyzing the data. For an IBM-type computer running MS-DOS, the small program approach is the most efficient due to the memory model employed. A menu group within the Microsoft Windows 3.0 environment was created to facilitate access to the microscope software. The Windows environment provided a pseudo-multitasking environment where several programs related to the operation of the microscope could be run simultaneously. Communication of data between programs was accomplished by reading and writing temporary files on a RAM disk. Programs to accomplish microscope control, data acquisition, and data viewing will be outlined below. The actual code for these programs is quite substantial and is provided as supplementary material rather than being included here as an appendix.

The basic microscope control program was coded in Microsoft QuickBasic 4.0. BASIC was used for the system control because of the ease of operation of interface boards in this programming language. This program offers a menu of choices for current/bias control, coarse approach, setup of scans over the surface, and two display routines. Each choice produced another menu or dialog to set up relevant parameters. The scan setup allowed the choice of operation mode (closed-loop or open-loop), time for the scan, and the input channel(s)

to record during the scan. The scans were 256 x 256 positions with an adjustable number of samples at each position between 1 and 16 points. Data was "smoothed" by linear averaging at each point rather than by using fast Fourier transforms and frequency filters. Data were displayed as 16-color images coded for height or other appropriate junction parameters. The topographic data could also be displayed in a three-dimensional line-scan representation. A menu built into the 16-color image display allowed zooming and sub-scans of the default imaging area. Image sizes could be adjusted from 3 nm x 3 nm to 120 nm x 120 nm with this program. The program obtained the display data by reading scratch files on the RAM disk written by the data retrieval program.

The data for each position, with multiple samples at each position, were stored in the on-board memory of the DAS-50 interface card. The interface board contained 1 Mb of local storage which relieved system i/o demands during high speed acquisition. A Microsoft FORTRAN 4.1 program was written to retrieve this data. The program read multiple data sets automatically and added the data for each position together to get a final array(s) of 256 x 256 points representing the average of several "scans". The data array(s) were saved as a scratch file for use by other analysis programs with a header to specify important parameters of the scan. This program also computed and stored the data for the 16-color images displayed by the main control program. Typical execution time to retrieve a data set of 4 samples per data point, add the samples together, calculate the 16 color image and write the raw data and the image data to temporary files, was 10 seconds.

In addition to the control program which provided quick and simple viewing for the purpose of quality control, a program was written to do more extensive data analysis including local filtering, plane subtraction, image display, and export of one-dimensional slices of the two-dimensional data sets. This program was a mix of Microsoft QuickBasic and FORTRAN routines. The main routine was written in BASIC, while FORTRAN was used for mathematical processing of the data. Algorithms in BASIC for performing local averaging ran 5-10 times slower than analogous code in FORTRAN. The start-up menu presented data import and export options and two display techniques. Display options were similar to the control program; however, more flexibility in processing was provided. Function key menus within each display routine allowed user-input scaling, local averaging, setup and run of a plane subtraction routine, image export to binary or plotter command files, and export of one-dimensional slices of the data. One-dimensional slices could be averaged over a number scan lines, and the direction of the slice was fully adjustable in 2 dimensions. This program was used to prepare data for export to specialized graphics rendering hardware by local filtering and plane subtraction. Data files to be exported were saved to temporary files that were read by one of two application visualization system (AVS) field preparation programs.

FORTRAN and in later versions, C, were the languages used for the AVS data preparation programs. One program was designed to compress the data at each point to 7 bits or 8 bits (C version) based on the maximum and minimum values in the image. The other program allowed interactive operation and displayed a histogram of the image data values. The user

selected a midpoint for the data and a window width for the data compression. Data compression to byte width allowed the image data to be understood by other computer hardware types, making it possible for a personal computer running MS-DOS to send data to a graphics supercomputer running the UNIX operating system.

High quality three-dimensional visualization of the STM images was achieved on a Stardent GS-2000 computer. The graphical output of this system is shown in the color plates in this thesis. All processing of data was done in AVS, a flexible graphical visualization environment. For the topographic data, AVS was used to convert the data into a three-dimensional surface which could be manipulated and viewed in real time. Data processing networks were developed within the AVS Network Editor to read data, filter data, and generate three-dimensional objects and two-dimensional color maps (images). Data filtering consisted of linear subsampling of the data and cropping the data. Data which had been subsampled by a factor of 2 to 4 could be used for interactive, three-dimensional visualization. Texture-mapping was used to map a color image onto the three-dimensional topographic data. This graphical technique places color values at the vertices describing the three-dimensional object. This visualization technique allows insightful viewing and presentation of simultaneous images of topography and conductance. Color prints of the results were generated on a Kodak XL7700C color printer.

Tip Construction:

Three basic tip types were developed for use with this microscope; silver microcrystal, platinum foil, and tungsten/tungsten oxide. Of these, the platinum foil and tungsten based tips provided resolution down to atomic sized features. The silver microcrystals were used for imaging surface features of larger size. The silver crystal tips were grown from a concentrated silver nitrate solution in exactly the same method as the seed crystals for the silver growth experiments were grown. The body of the tip was sealed in glass to prevent silver deposition except at the exposed platinum disk of 125 μm . Platinum tips were prepared by cutting platinum foil with a pair of sharp scissors. Each cut was about 2-3 mm long and tapered to a narrow sheared end. These small foil wedges were mounted on a 18 gauge copper wire with silver epoxy or nickel paint. The silver epoxy provided slightly better adhesion, at the cost of an annealing step. Tungsten tips were fabricated by etching in 3M NaOH under galvanostatic conditions. The end of an 18 gauge tungsten wire was protected by a short teflon tube⁷⁷. Etching to a neck above this sheath was accomplished by a d.c. current of 50 to 70 mA, at voltage limit 25 V. The neck was broken, leaving a sharp tip, with a square wave current of ± 5 mA with voltage magnitude 2 V and dwell time 3 ms. This finishing step leaves a doped thin layer of tungsten oxide over the end of the tip⁷⁸. The tungsten oxide prepared in this manner is a non-stoichiometric bronze, $(\text{H},\text{Na})_{x<1}\text{WO}_3$ ⁷⁹, hereafter referred to as "WOx". All tips were checked for gross shape with a 100x microscope. Usually, tips which appeared very blunt did not work in the microscope, making gross checks worthwhile.

Sample Preparation:

The samples prepared for this work were mounted on gold sockets. The evaporated gold films were deposited on glass microscope slides to thicknesses of 1000 Å in the Majda⁸⁰ research lab. The glass microscope slides were broken into small shards, which were mounted on the socket with epoxy. A strip of nickel paint was used to provide electrical contact between the gold film on the top of the glass microscope slide and the gold socket. After assembly, the gold samples were cleaned by rinsing with n-hexane. Platinum foil samples were spot welded onto an 18 gauge platinum wire. An entirely platinum part allowed flame cleaning and quenching in concentrated HCl. After the acid clean, the platinum assembly was heated and quenched in ultrapure water to remove residual sodium. The wire was plugged into a gold socket during microscope assembly. Highly oriented pyrolytic graphite⁸¹ (HOPG) samples were attached to the top of a gold socket with nickel paint. The samples were cleaved with adhesive tape to provide a flat and fresh surface for imaging.

System Calibration:

The microscope was calibrated for both lateral drift and scan size by some simple experiments. For the parallel configuration, the scan size changed with changing tip length, so calibrations were required when the tip length changed significantly. Templates were used for tip cutting to reduce length variations to the order of 5%. Scan size was calibrated by imaging freshly cleaved HOPG. Fast calibration images with minimal drift distortion were acquired with the microscope

operating in open-loop mode. A calibration image showing atomic-scale contours is shown in color plate 1. Lateral drift of the samples varied depending on the microscope configuration and the time elapsed from assembly. Lateral drift was measured by taking a series of images at known time intervals. For the parallel configuration, initial drift rates ranges from very high to 5-10 nm per minute. Drifts were classified as very high when two sequential 100 x 100 nm images failed to show any common features. The initial drift rates for the coaxial configuration were about an order of magnitude lower. After 6-12 hours of operation the parallel configuration approached the lateral stability of the coaxial configuration. Low drift rates for the microscope were in the range of 1-2 Å per minute.

Vertical checks of the microscope response were conducted by observing single and multiple steps on the basal plane of HOPG. Tunneling current calibration was done with dummy tunneling junctions of known resistance. The conductance signal was corrected for instrumental response by a simple nulling scheme. The high frequency perturbation used for the bias modulation conductance measurement produced a modest instrumental pickup. The bulk of this signal is due to capacitive coupling which is 90° out-of-phase with respect to the tunneling current modulation. The detection phase angle of the lock-in amplifier was adjusted to place the capacitive coupling on the imaginary detection axis. The phase adjustment was conducted with the tip just out of tunneling range. With the lock-in properly nulled, the tip was brought within tunneling range and the real component was used as the tunneling

conductance. For a correct null, the imaginary signal was independent of the tunneling current magnitude.

Results and Discussion:

The results presented in this section cover a range of tip types, sample types, and imaging techniques. The data were acquired over the 10-month development period of the microscope. Since the instrument was constructed in the laboratory, a considerable portion of the time for the project was spent on developing the software and hardware for the STM. The studies reported here are a range of results used in the design modification and certification of the capabilities of the microscope. The significant contributions by the work to date are in the areas of imaging with novel tip materials, and in the application of simultaneous imaging and visualization.

Gold Surfaces and Gold With Cadmium Sulfide:

Evaporated gold surfaces were one of the first sample types that were tried in our microscope. These films are relatively simple to prepare and have been documented elsewhere⁸⁰. STM images of gold evaporated films have been previously reported⁷⁴. One major drawback of gold surfaces exposed to air is their tendency to adsorb contaminants (primarily hydrocarbons and sulfur compounds) from the laboratory environment. This posed no significant problems in initial imaging experiments, since the major concern was the resolution of gross

topographic features. For films exposed to the laboratory environment for up to a couple of days, the STM behaved in a stable manner. Apparently, thin films of air-based contaminants do not degrade the behavior of the tunneling junction. After a few days of exposure to ambient conditions, the quality of the tunneling junction prepared with the gold film was significantly degraded. This was manifested in an unstable vertical tip position over the surface. Fluctuations of 50 nm to 200 nm were often observed under these conditions. Stable junctions were (re-)attained after rinsing these surfaces with n-hexane; indicating that the destabilizing contaminants were largely hydrocarbons soluble in n-hexane. The results reported here were obtained on films cleaned in this manner before microscope assembly.

Illustration 39 shows a pseudo-three-dimensional representation of an image of a gold surface. This picture was constructed by one of the data display routines running on the STM control computer and plotted on a Hewlett-Packard HP7475A plotter. The first objective of the microscope was to resolve surface features of a few nanometers in size and larger. As can be seen, the rolling hill topography of evaporated gold films is well suited for testing this ability. Silver crystal tips prepared by growing small (approximately 100 μm across) crystals from concentrated silver nitrate provided good quality images on these length-scales. These results compare reasonably with other results of gold films in air or condensed media. Color plate 2 shows a three-dimensional surface of this data generated by a graphics supercomputer. These tips are suitable for the study of relatively large surface features.

An image acquired of the same film with a platinum foil tip is shown in color plate 3. In general, the platinum tips were better at recognizing smaller surface features in x,y, and z. The resolution of the two tip materials illustrates one of the problems with the operation of an STM. Poor resolution STM images are observed when the effective tunneling area becomes large. This is because the image is a convolution of the contours of the tip and sample local density of states. A blunt tip has a slowly varying lateral local density of states, so an image acquired with a blunt tip shows poor lateral resolution. When the tip shape is blurred by dynamic surface processes, the tip appears blunt and resolution again decreases. The silver microcrystal tips could have blunt regions resulting from rounding of the facet edges on a microscopic scale. It is also possible that the tips could have resolution problems due to the low activation barrier to surface diffusion (see chapter 1). Usually, high-melting or even refractory metals or alloys are used as tip materials^{52,57-62}. Silver crystal, or "soft", tips are useful primarily in imaging rather large features on surfaces. One unique advantage of these tips their is easy preparation and their reusability. If a silver crystal tip is too blunt for use, the crystal at the end can be removed and regrown in a few minutes.

Surface averaged, or one-dimensional, tunneling spectroscopy was used to study the band structure of gold films and gold with a thick film of electrodeposited CdS. The tips used for the spectroscopy were platinum foil tips. The spectroscopy measurements were conducted by the application of a 3-30 mV a.c. bias perturbation at a frequency of 3 kHz.

The frequency of the perturbation was significantly faster than the response speed of the vertical control feedback loop. This ensured that the d.c. tunneling current could be held constant through feedback on the vertical position while the spectroscopic measurements occurred. Under constant tunneling current conditions, the bias perturbation produces a current response proportional to the tunneling junction a.c. conductance, (illustration 40). This is another method to measure the quantity $(di/dV)_{V=\text{const.}}$. Many workers⁶⁰ measure this quantity by measuring current-voltage curves at constant separation and use numerical differentiation to obtain $(di/dV)_{V=\text{const.}}$.

The tunneling junction a.c. conductance was normalized by the d.c. conductance to remove contributions to the spectra from first order area and transmission factors. This is similar to the approach of Jaklevic and Kaiser⁸² in their measurement of Au and Pd surface-electronic structure. Their approach maintains a constant d.c. conductance while changing the applied bias through adjustments of the d.c. tunneling current set point. The normalized conductance for a bare Au surface is shown in illustration 41. The physical quantity measured by tunneling spectroscopy is composed of several components. Along with the traditional interpretation of a signal proportional to the local density of the occupied and unoccupied states, the normalized conductance signal can vary from tip-to-tip due to higher order area contributions and the normalized conductance shows a dependence on the local surface work function.

One major contribution to the tunneling signal is due to the number density of states involved in the tunneling process. When both

the sample and tip are metals, the dominant current should result from the tunneling of an electron from the negative metal to the positive metal. For a positive sample bias, electrons near the Fermi level of the tip will elastically tunnel into the sample's unoccupied states. For a negative sample bias, electrons will tunnel from the Fermi level of the sample into the tip conduction states. The highest occupied electronic energy states in the negative material (either tip or sample) will provide the predominant tunneling signal because these states have the lowest tunneling barrier. Information regarding the number density of lower electronic energy occupied states is clouded because of the higher tunneling barrier. As a result, only sharp changes in the number density of occupied states at a particular energy may be observed, along a varying background.

The changes in the number density of unoccupied states are significantly more apparent in the normalized conductance. This is a result of the approximately constant number of occupied states at the Fermi level. As the energetic position of the highest energy occupied level changes, the number density of unoccupied states near this energy is probed. There is a good discussion of the issue and some of the trade-offs involved in the reviews by Hamers⁶⁰ and by Griffith and Kochanski⁶². The major conclusion is that pronounced changes in the conductance as a function of bias are indicative of tunneling junction local density of states changes. The shape of the spectra, however, are difficult to correlate with the exact electronic state spectra of the individual materials composing the tunneling junction unless an accurate surface band structure of either the tip or sample is known *a priori*.

When a semiconductor becomes part of the tunneling junction, the presence of a forbidden gap enhances the information obtained regarding the occupied states. It is possible to observe changes in the number density of occupied states below the Fermi level of the semiconductor when the Fermi level lies above the valence band edge. Spectroscopic measurements of semiconductor samples with a metal probe tip reveal the positions of the conduction and valence band^{73,82-85}. The valence band appears prominently in the normalized conductance spectrum because of the high number of occupied states that can produce electrons that tunnel into the tip's unoccupied states. After the initial rise in conductance due to the onset of tunneling from the valence band, the most pronounced features would arise from changes in the density of unoccupied states in the tip, all other things being equal.

Illustration 42 shows the normalized conductance signal for a thin film of CdS on a gold surface. The CdS film was deposited electrochemically by reducing thiosulfate in the presence of Cd^{2+} . The presence of small "isolated" CdS grains on the surface was verified by overtone RAMAN⁸⁶ spectroscopy. The vertical stability of the tunneling junction with this film was very poor. No stable, reproducible images of the surface were recorded. However, the surface-averaged conductance signals were self-consistent and reproducible. Surface-averaged conductance was measured by scanning the tip over the surface with the conductance detection channel set at a time constant of 3 seconds. When comparing the spectra, illustrations 41 and 42, there are major differences which can be attributed to the addition of a CdS film and band structure with a forbidden gap to the system. The band gap of bulk

CdS is 2.42 eV, CdS particles of small size display wider band gaps^{87,88}. The approximately 3 eV gap between the regions labeled as valence and conduction bands is sensible for this surface deposit.

These experiments with gold evaporated films allowed simple checks of drift and tip preparation schemes. The work in one-dimensional spectroscopy laid the foundation for instrumental design for the spatially resolved spectroscopic measurements. The results here are consistent with the results obtained by previous work on gold surfaces and other semiconductor surfaces. Kuk and Silverman⁹⁰ report similar spectra to our result for the bare gold surface, both our and their results differ in appearance on the positive sample side from the work by Kaiser and Jaklevic⁸⁰. However, Kaiser and Jaklevic point out that the feature they observe is probably due to a surface state, so the inconsistency may be explained by sample preparation differences. Although direct measurements of CdS band structure have not been reported, work by several groups on semiconductor substrates has observed band-gap type features^{73,82-85}.

Platinum Surfaces:

Platinum surfaces were imaged in air with platinum foil or tungsten based tips. The gross surface structure and the presence of local work function changes on surface "facets" were studied. Simultaneous imaging techniques produced new information regarding the properties of polycrystalline platinum surfaces exposed to air. A high resolution topograph of a typical platinum surface is shown in color

plate 4. Steps, terraces, and a canyon provide a typical microscopic view of the platinum surface. However, the information about a realistic surface which can be obtained from this type of data, is limited. For example, the presence of airborne contaminants is not revealed. It is possible that this metal surface is free of surface contamination, but not likely. This is a major drawback of experiments that measure only topographic information using the STM. Topographic data obtained on typical surfaces does not usually contain sufficient information to determine the molecular or chemical identities of features on the surface.

This type of drawback exists for many commercially available STM systems. This was one of motivations for developing an STM/S instrument within our lab. The instrument designed and constructed as part of this research is tailored for experiments related to discerning certain types of chemical differences on realistic surfaces. Our approach uses the simultaneous measurement of multiple tunnel-junction observables as a means of performing this type of recognition. Color plate 5 shows two renderings of the same topographic data which illustrates this idea. The top picture is a three-dimensional representation of the topography of a platinum surface, imaged in air; while the bottom picture is a combination of this topographic data with color-coded data from the a.c. conductance at each point on the surface. The bottom picture is obtained by texture mapping the conductance image onto the three-dimensional topography. The additional information regarding relative conductance differences between several surface regions is then easy to visualize.

Theoretical expressions (like equation 24) for the tunneling conductance signal under conditions of constant current reveal that two major components have contributions which can cause the relative changes in conductance shown in color plate 5. One possibility is that the local density of electronic states at this sample bias is different from one surface plane to another (the first term in the numerator in equation 24). This is the traditional interpretation of STS images, namely that spatially varying conductance signals are attributed to changes in the local density of electronic states. Another possible explanation of the changes in relative conductance over the surface is a localized change in surface dipole, affecting local tunneling barrier heights (as mentioned earlier, $A(V_g)/B(V_g)$ in equation 24 is related to the local barrier). Under appropriate normalization for tunnel junction d.c. conductance, the small-signal conductance is linearly dependent on local barrier changes. The dependence of the normalized a.c. conductance on the number density of states is significantly less than linear, as evidenced by the small changes in the quantity when studying semiconducting samples. In the presence of local barrier changes, therefore, local changes in the number density of states will be difficult to detect because of their small contribution to normalized conductance signals.

In light of this, we attribute the relative variation in conductance of 30% in color plate 5 to local work function changes. Differentiating equation 23 and employing a trapezoidal barrier, this relative conductance change correlates to a variation of about 1.2 eV in the tunneling barrier. A platinum surface exposed to airborne

contaminants could readily acquire surface species capable of producing surface dipole changes of this magnitude^{91,92}. Adsorbates are indicated in this case since the variation in work function of clean platinum surface planes ($\langle 111 \rangle$ to $\langle 100 \rangle$) are about a factor of 5 to 10 too small. Surface work function changes observed on platinum surfaces exposed to aromatic adsorbates are on the same order as the changes observed here⁹².

More carefully controlled experimental conditions are required to establish the chemical nature of the adsorbate and verify these conclusions. However, this application of simultaneous imaging to obtain surface chemical information shows promise. This example highlights the utility of multiple imaging techniques at a single junction bias. Surface conductance changes can be directly used to differentiate "bumps" and surface features on the basis of local work function changes. Promising work in our laboratory is continuing in the area of recognition of semiconductor clusters on rough metal surfaces.

Highly Oriented Pyrolytic Graphite Samples:

The imaging described in the previous section was performed at one bias. Under those conditions, the conductance signal is a useful diagnostic; however, its utility as a "spectroscopy" tool is only realized when the simultaneous images are acquired at a range of biases. Data on a highly oriented pyrolytic graphite (HOPG) surface exposed to air were acquired over the sample bias range of -0.5 to 0.4 eV. These images were acquired over the course of about 30 minutes and captured a

region of the surface with small steps separated by terraces. Color plate 6 shows one simultaneous image with topography and texture-mapped conductance at one bias.

Stepped regions like this are uncommon on freshly cleaved HOPG surfaces. Usually, approach of the tip and imaging revealed perfectly flat terraces from 500 nm to 1.0 μm across. Massive defects, see color plate 7, and steps as in color plate 6 were found during active searches of the surface for such features. These surface features turned up over the course of systematic searches for surface defects that lasted for a few months of microscope operation and testing. The defect region in color plate 7 appears to be a result of a twist boundary. There are two major domains to the right and left. At their intersection, step and terrace lines slew off in a range of directions, of which only a fraction are consistent with the hexagonal symmetry of the surface.

Quantitative spectroscopic information for the simple step and terrace system in color plate 6 can be obtained by analysis of the relative conductance at each surface position. This is accomplished by an analysis program that takes the two-dimensional image data and extracts the scan line values. This program can use a single scan line or average over several lines to increase the signal to noise ratio. A plot of the vertical and conductance signal for one bias is shown in illustration 43. The vertical scale, primary y axis, is significantly magnified with respect to the surface position on the x axis. This plot is representative of the data; there are terrace regions with slight planar misorientation and steps between the terraces.

The conductance signal at the step is significantly higher than the terrace conductance signal. To convert the set of images into specific spectroscopic information for particular surface features, the following data processing was performed. For each image, data like that shown in illustration 43 were extracted. Then, the conductance at the step region and the conductance over the terrace region were normalized by the d.c. conductance. Finally, the data are compared for the terraces and the steps; illustration 44 displays the normalized conductance data obtained by analyzing all the images. The "v" shape of the two sets of values indicates that the normalized conductance has a roughly linear dependence on sample bias over this range of bias. This linear change in normalized conductance indicates that the major difference between the step and the terrace lies in the local work function. The ratio between local step work function and terrace work function is obtained by dividing the slope of the step data by the slope of terrace data. Assuming that bulk surface values for the work function are close to the terrace value, the local work function at the step is lower by 1 ± 0.5 V (95% confidence values from linear fits to the data).

The sign of the local work function change agrees with theoretical models of electron density at a step in a jellium metal⁹³⁻⁹⁵. Near a step in the surface, electronic density spills outward parallel to the plane of the surface, creating a net negative charge at the base of the step and a net positive charge at the top of the step⁹⁶. From illustration 43, we see the spatial extent of the lower local work function is on the order of a few nanometers, which indicates a modestly

delocalized perturbation to the surface dipole. The component of this charge separation at the step that lies normal to the surface is aligned against the jellium surface dipole, reducing the work function locally around the step⁹⁵. However, the calculations by Thompson and Huntington⁹⁶ for steps on a sodium surface suggest a locally induced potential change around 0.1 eV, about an order of magnitude less than observed here. Besocke et al.⁹⁷ present measurements of work functions for stepped metal surfaces of tungsten, silver and platinum. Their observations are consistent in magnitude with the calculation by Thompson and Huntington. They do point out that the variation observed in step induced work function varies significantly with the metal. We propose that the large inter-plane spacing is producing higher than expected work function changes at the steps. Since graphite is a rather unique metal, this could still be a reasonable explanation.

Another possible explanation is that the jellium model is not appropriate to describe this experimental result. In this case, we would need to apply a theory of a surface and steps from a more molecular, localized standpoint. However, the behavior over energy (illustration 44) tends to rule out energetically localized states. A final possible explanation is the presence of chemical inhomogeneity at the step, like the platinum surface. This has been eliminated as a strong contender because evidence gathered while acquiring all of the data in illustration 44 suggests that sheets were stripped off the surface during the course of the experiment. This effectively presented a fresh, uncontaminated surface with steps at the start of several of the scans. Additionally, other experiments in our laboratory have found

that stepped HOPG surfaces are quite resistant to chemical attack, even oxidation⁹⁸.

The differences between the terrace and step signal in illustration 44 is quite striking. There is a more subtle difference between the relative conductance signals between the terraces themselves. The difference is quite obvious in color plate 6, where one terrace has a bluish cast while the other is yellowish. The bluish color is indicative of low relative conductance and a relatively higher work function or lower number density of surface electronic states. For graphite, a material where the interactions between the sheets are relatively small, stacking faults may be common. It is quite probable that a stacking fault producing a sequence of ...abcaba would produce a surface that was slightly different electronically than an unfaulted surface layer ...abcabc. This hypothesis is supported by the significant change demonstrated in graphite band structure calculations⁹⁹ when a neighboring layer is allowed to interact with a graphite sheet. The experimental percentage difference between the two terrace types in the conductance is approximately 5%. These two terrace types were observed multiple times during the systematic search of the HOPG samples for defects. Only two relative conductance levels were observed in these studies, supporting the faulted vs unfaulted surface model.

Summary:

In this chapter, the surfaces and results have spanned the range from reproducing other work to the application of simultaneous imaging techniques to platinum and HOPG. The availability of silver microcrystal tips opens possibilities for unique quality control by *in-situ* tip modification via crystal growth. Simultaneous imaging of platinum surfaces has provided a glimpse at surface region differences which are nominally not apparent to STM. Spectroscopic simultaneous imaging techniques have shown local electronic changes at steps on HOPG. Finally, terrace stacking faults have been observed, again a detection of subtle surface differences not apparent to traditional scanning tunneling microscopy.

illustration 34: a) Schematic of band structure of a homogeneous junction with no applied bias. Shaded areas denote occupied states; for metals, the overlap of the conduction band with the valence band results in delocalized electronic states near the Fermi energy, E_f . For small s , overlap of delocalized electronic states between the materials will allow electron tunneling from tip to sample or vice versa. b) If the sample is at a positive bias (V_s) with respect to the tip the net electric field will drive a net flow of electrons from tip to sample. Since the tunneling probability is roughly exponentially dependant on the height of the potential barrier, the highest energy electrons (near E_f of the tip) will be the major contributors to the net flow of electrons in this case. This results in a roughly local probe of the unoccupied states in the sample around the energy $E_{f(s)} + eV_s$.

illustration 35: Physical mount for microscope apparatus. The plywood sheet is suspended by elastic cords. An acoustic/thermal shielding box rests on the plywood sheet. Inside the box, a Newport 3' x 2' optical table sits on 4 air-filled bladders. The microscope electronics and local acoustic shielding box are mounted to the top of the optical table.

illustration 36: Parallel configuration in a simplified side view. In all, 6 contact points by ball bearings were used to position the tilting plane. Two of the three for vertical control are shown here. There are two bolts used for gross separation control. Once locked, these bolts were not moved. Coarse approach was accomplished by shortening an 80 thread-per-inch screw, producing rotation of the tilt plane at the other ball bearing point contacts. The wires associated with the piezoelectric elements and the tip were rigidly mounted to the optical table. The sample wire is a light-weight wire to prevent transmission of residual stress and vibrations.

illustration 37: Cross-section of coaxial configuration. The scanning piezo element (Burleigh PZ-81) has a central bore large enough to accommodate the coarse PZT pusher. A brass fitting on the top of the coarse piezo element is connected to a rotationless micrometer spindle. Coarse mechanical approach is accomplished by the micrometer which moves the coarse piezo within the scanning element. The tip holder is affixed to the end of the coarse PZT with a magnet. Samples may be replaced from the bottom side of the MACOR holder without removing the sample cap.

illustration 38: Configuration of piezoelectric elements in the Burleigh scanning PZT. The side views show the symmetric mode that produces z translation of the tip and the asymmetric mode that produces x translation of the tip. The transformations were identical to the orthogonal modes of the appropriate symmetry point group, C_{2v} .

illustration 39: Line representation of a gold film as viewed by a silver microcrystal tip. The imaging area is 100 nm x 100 nm. The scale bar to the left is 5 nm high. Every fourth scan line is shown here to reduce clutter. On a monitor screen, every other scan line produces an acceptable picture. Scan parameters for this image; scan time 2 minutes, sample bias 0.25 V, tunneling current 0.2 nA, peak-to-valley height 80 nm. Two local average passes were run on the data before generating the figure.

illustration 40: Sketch of conductance measurements. A constant bias is applied, V_s ; with active feedback, i_t , is maintained. A small bias perturbation dV is applied and the response di is measured by a lock-in amplifier. As long as dV is small compared to V_s the quantity $(di/dV)_{V=V_s}$ is obtained. Typically, we use $dV = 3 - 30$ mV and $V_s = 0.1 - 2$ V.

illustration 41: Tunneling junction conductance spectrum of a bare gold surface acquired at room temperature. The normalization is obtained by multiplying the lock-in response by the absolute value of the bias and dividing by the tunneling current.

Pt/air/CdS/Au Junction Normalized
Conductance vs. Bias

illustration 42: Tunneling junction spectrum of gold with a thin film of CdS. Normalization produces the same units as in illustration 41. Comparing to illustration 41, the new features are the wider, flatter band at positive bias and the sharp signal increase at sample bias -2.3 V. Both features are consistent with the addition of a material with band structure similar to cadmium sulfide. The very negative pinning of the CdS valence band (VB) with respect to the Fermi level of gold has also been observed elsewhere⁸⁹.

Linescans for Topography and Conductance

illustration 43: Topography and conductance signals averaged over 20 lines for a step and terrace region of HOPG. This data is extracted from a simultaneous image acquired at sample bias -0.1 V and tunneling current 1 nA. The topography data is exaggerated by about 15 times with respect to the horizontal (distance) axis. One single-layer step and one two-layer step is visible; the two-layer step appears to separate two different terrace types. The actual misorientation angle between the terraces at left and at right is about 2° . The differences between step and terrace conductance are apparent as well as the conductance difference.

illustration 44: Voltage behavior of normalized conductance over a small bias window. The almost linear increase in normalized conductance with bias is indicative of constant barrier height and relatively small variation in local electronic state density. Steps of 1 to 2 HOPG c-spacings are compared to terraces. The majority of the difference appears to result from local work function differences. The minor, but observable difference in slopes for the terrace and the step data are consistent with a 1 ± 0.5 V lower work function at the steps.

Color Plate 1: Open-loop mode calibration image of highly oriented pyrolytic graphite (HOPG) acquired with a WOX tip. The observed corrugations are a result of current variation during the scan. Due to drift during image acquisition, the corrugations are distorted slightly from their ideal hexagonal shape. This is not readily apparent from the image here; however, it places significant bars on the absolute calibration of the image size, 2.6 nm x 2.6 nm ($\pm$ 3 nm per side). By using the tip length, geometry of tip holder and magnitude of signal to the scan element, the image is calculated to be 2.5 nm x 2.5 nm. The data has a grayscale image of the current texture-mapped onto the three-dimensional physical map of the current. The data has been downsized by a factor of 2, the geometric data is illuminated with one light and Gouraud shading is used in the rendering.

Color Plate 2: Closed-loop mode image of a gold surface by a silver crystal tip. The image size is 100 x 100 nm with a total peak-to-valley height of 80 nm. The large hillock in the foreground accounts for most of the vertical variation in the image. Parameters for this data: scan time, 2 minutes; average current, 0.2 nA; sample bias, 0.25 V; 8 samples/point. A 3 x 3 Gaussian convolution filter (low pass) with focus 0.5 is applied to reduce rendering noise which is still visible as the small, regular hatching in some parts of the image. This image is rendered with 2 lights; data downsized by a factor of 2 and with Phong shading.

Gold Imaged by Silver Tip

Color Plate 3: Closed-loop mode image of a gold surface acquired with a platinum tip. The image size is 100 x 100 nm with a total peak-to-valley height of 5 nm. The vertical enhancement between this data and the previous image (color plate 2) is 6.4 times. Parameters for this data: scan time, 30 seconds; average current, 1.0 nA; sample bias, -0.25 V; 4 samples/point. A 3 x 3 Gaussian convolution filter (low pass) with focus 0.5 is applied to reduce rendering noise. This image is rendered with 2 lights; data downsized by a factor of 2 and with Phong shading.

Color Plate 4: Closed-loop mode image of a platinum surface acquired by a platinum tip. The image size is 120 x 120 nm with a total peak-to-valley height of 14 nm. Parameters for this data: scan time, 1 minute; average current, 1.0 nA; sample bias, 0.25 V; 8 samples/point. A 3 x 3 Gaussian convolution filter (low pass) with focus 1.0 is applied to reduce rendering noise. This image is rendered with 2 lights; data downsized by a factor of 2 and with Phong shading.

Platinum Imaged by Platinum Tip

Color Plate 5: Top object. Closed-loop mode image of a platinum surface acquired by a tungsten tip. The image size is 100 x 100 nm with a total peak-to-valley height of 82 nm. Parameters for this data: scan time, 5 minutes; average current, 3 nA; sample bias, 0.2 V; 8 samples/point; bias perturbation 10 mV at 14 kHz. A 3 x 3 Gaussian convolution filter (low pass) with focus 1.0 is applied to reduce rendering noise.

Bottom object. Topographic data as in the top object with a texture map of the simultaneously acquired conductance signal. The conductance signal is color coded, yellow for high conductance and blue for low conductance. This means that the regions which appear bluish have a higher work function. This scene is rendered with 2 lights; data downsized by a factor of 4 and with Phong shading.

Platinum Surface With and Without
Conductance Texture

Color Plate 6: Closed-loop mode topographic data and conductance texture map of HOPG acquired with a WOx tip. As in the previous color plate the conductance is color coded with yellow for high conductance and blue for low conductance. The image size is 50 x 50 nm with a total peak-to-valley height of 5 nm. Parameters for this data: scan time, 5 minutes; average current, 1 nA; sample bias, -0.3 V; 8 samples/point; bias perturbation 10 mV at 14 kHz. A 3 x 3 Gaussian convolution filter (low pass) with focus 1.0 is applied to reduce rendering noise. This image is rendered with 2 lights; data downsized by a factor of 2 and with Phong shading.

Stepped HOPG Surface With • Conductance Texture

Color Plate 7: Closed-loop mode image of a HOPG surface acquired with a WOX tip. The image size is 50 x 50 nm with a total peak-to-valley height of 6 nm. This is a snapshot of a defect between two flat sheets of graphite. The large buckle/step features which run off in three directions from the center of the region vary in height from 2 to 4 nm. Parameters for this data: scan time, 2 minutes; average current, 1.0 nA; sample bias, 0.2 V; 8 samples/point. A 3 x 3 Gaussian convolution filter (low pass) with focus 0.5 is applied to reduce rendering noise. This image is rendered with 2 lights; data downsized by a factor of 2 and with Phong shading.

HOPG Large Defect Region

CHAPTER 4

SUMMARY

This chapter summarizes the results and discussions presented in the previous chapters. Where possible without sacrificing brevity, quantitative results will be reiterated here; for more detail, please consult the appropriate chapter.

The synthesis and characterization of low-defect density silver/aqueous silver nitrate interfaces were performed. However, low-activity surfaces similar to those reported previously by the researchers at the Bulgarian Academy of Sciences were not observed. Instead, we found that capillary growth techniques produced low-index silver surfaces which were either inactive or which demonstrated activity predominantly at one defect site. Inactive silver surfaces have not been reported previously. Study of the inert and slightly active surfaces allowed determination of quantities which have previously been experimentally problematic. On the inert surfaces, impedance spectroscopy was used to study water dipole reorientation at the interface and surface adsorption of silver ad-species. The enthalpy of reorganization of water dipoles at the interface was calculated to be 24.5 kJ/mol. The typical occupation of adsorbed silver atoms is around 1 atom per 400 surface atoms at room temperature. Our observed nucleation rates obtained for the first time at inert surfaces and the previously-reported nucleation rates for silver clusters have been

interpreted using a model which incorporates site-dependent surface free energy terms and the stabilization of clusters at defect sites. We find that the "typical" surface defect studied by this work and previous work stabilizes a critical cluster by a small percentage of the total surface energy of the low-index silver surface. However, this 5% change produces an enhancement of up to 8 orders of magnitude in nucleation rate.

Unlike the researchers at the Bulgarian Academy of Sciences, we were apparently able to successfully prepare silver surfaces that had a mixture of active and inactive regions. The active regions contained a single defect which dominated the reactivity of that region. These defects were apparently formed at the crystal wall/capillary wall interface. After a few experiments, their presence was easy to detect because of their impact on the total observed growth rate. Growth on these small active regions proceeded as a deterministic series of small growth events with distinctive shapes. The rate determining step in the nucleation and growth process of these events was the surface self-diffusion of silver atoms at the interface. We determined surface diffusion coefficients for this surface moiety at two temperatures; at $T = 20^\circ \text{C}$, we found $D_s = (1.2 \pm 0.3) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, and at $T = 50^\circ \text{C}$, $D_s = (2.5 \pm 0.9) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. One interesting direction for further study on this system would be the use of defect site location information as a guide to the study of the defect surface structure. Surface sites with different cluster nucleation rates (for which there is some evidence, such as our wall defects and the sites on the "inert"

surfaces prepared by Budevski et al.) could be used to correlate surface structure with energetics and reactivity.

The computational modeling of growing surfaces was one of the more interesting parts of this thesis work. We were able to show that computer modeling of the growth of a circular layer onto an elliptical substrate was feasible, and the results of these simulations were used to develop positional analysis routines. These routines were largely successful in determining the nucleation site of a growth event given the time dependence of the growth reaction rate. For a macroscopic crystal surface within a small capillary tube, the calculations showed that it is possible to locate a microscopic nucleation site with fair precision. Typically, the mean deviation from the calculated site and the actual site was between 400 and 900 nm. This approach is one way to bridge the gap between macroscopically observed reactivity and microscopic probes that can study surface structure. Experimentally observed growth events were modeled in a similar manner. One-dimensional hopping simulations were used to study hopping statistics under long diffusion lengths and low concentrations from an equilibrium concentration region. A linear relation was discovered between the inverse of the simulation length and the scaling of the apparent diffusion coefficient. This relation allowed smaller simulations, accessible to simple computers, to accurately model diffusion over macroscopic silver crystal surfaces.

For our scanning tunneling microscope/spectrometer, the surfaces and results have spanned the range from reproducing other work to the application of simultaneous imaging techniques to platinum and HOPG. In

this work, we applied silver crystal growth techniques to develop a reusable tip. The availability of these silver microcrystal tips opens possibilities for unique quality control by *in-situ* tip modification via crystal growth. One extremely challenging part of working in such a popular field as STM is performing work which stands out as unique. We feel that by constructing our own microscope, we have been able to optimize our tool for simultaneous acquisition of topographic and conductance data. The optimization process itself proved a considerable task during which we encountered artifacts inherent to these instruments that many novice users of commercially available systems may not consider.

Simultaneous imaging and visualization of combined topographic and conductance data of platinum surfaces has provided a glimpse at surface region differences which are nominally not apparent to typical STM instruments. These surface region differences appear as changes in local work function. These relative work function changes are around 30% over the entire surface. Spectroscopic simultaneous imaging techniques have shown local electronic changes at steps on HOPG. The observed experimental local work function change is 1 ± 0.5 V; this quantity is larger than expected. Hopefully, further work of this type will lead to a better understanding of the electronic properties of steps at surfaces and interfaces. On HOPG, terrace stacking faults have also been observed; again, a detection of subtle surface differences not apparent to traditional scanning tunneling microscopy. Application of complementary techniques such as scanning conductance measurements to

STM-based instruments appears to be a very promising addition to the tools for study of surfaces and interfaces.

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APPENDIX A

source code for silver growth experiments:

GROWSAMP.BAS source code:

WRKSPCE.BAS source code:

```
DECLARE SUB CONTCON ()
DECLARE SUB IMTEST ()
DECLARE SUB PPGM ()
DECLARE SUB ERRHAND (ET)
DECLARE SUB CINST ()
DECLARE SUB POTLINC ()
DECLARE SUB POTLDEC ()
DECLARE SUB ICOLLECT (FLAG%)
DECLARE SUB IPLOT ()
DECLARE SUB RESTPOT
DECLARE SUB POTLSET ()
DECLARE SUB LABSETUP (rf!)
DECLARE FUNCTION ADCONV! (CH%)
DECLARE SUB OSCOFF0
DECLARE SUB OSCOFF1
DECLARE SUB OSCON0
DECLARE SUB CHGFREQ ()
DECLARE FUNCTION DETSENS! ()
DECLARE FUNCTION LOG10! (X!)
DECLARE SUB STWAIT ()
DECLARE FUNCTION GETVAL! (SS%, CH%)
REM $DYNAMIC
DIM SHARED addat0(30000) AS INTEGER
DIM addat1(30000) AS INTEGER
DIM addat2(30000) AS INTEGER
DIM addat3(30000) AS INTEGER
DIM addat4(30000) AS INTEGER
DIM addat5(30000) AS INTEGER
DIM addat6(30000) AS INTEGER
DIM addat7(30000) AS INTEGER

CONST PI = 3.141593
DIM SHARED DPOT%, POFFS%
DIM SHARED segarr(0 TO 7) AS INTEGER, fl$(7)
DIM SEGAR(0 TO 7) AS INTEGER
DEFINT A-Z
'This program is an interactive data acquisition program.
'The user can specify an applied potential, turn the oscillator on
'or off, and convert and save the current at various sampling rates.
```

'Impedence scans and double pulse experiments can be conducted.
 'the main module is the option module while the impedance scan program
 'is in another module, IMTEST.

```

OUT &H2AF, &H80      ' clear and configure labmaster parallel ports
CALL OSCOFF0         ' set to startup, low gain, oscillator off,
DIGOUT% = 1          ' default cell, and DAC0 at zero output
SENS% = 0
OSC% = 0
OUT &H2A1, 0
OUT &H2A0, 0
POFFS% = CINT(ADCONV(6) * 10 / .0481)  ' measure internal potential
offset.
MENUPOINT:
CLS
PRINT "      Menu:"
PRINT "      1=Set and verify applied potential"
PRINT "      2=increment potential"
PRINT "      3=decrement potential"
PRINT "      4=change sensitivity"
PRINT "      5=turn oscillator on\off"
PRINT "      6=take current measurement"
PRINT "      7=switch active cell"
PRINT "      8=potential pulse experiment"
PRINT "      9=measure rest potential"
PRINT "     10=make impedance scan"
PRINT "     11=exit program"
PRINT "     12=continuous channel conversion"
INPUT CH%
SELECT CASE CH%
  CASE 1
    CALL POTLSET: pot1! = ADCONV!(6) * 10
    PRINT "The applied potential is now ";
    PRINT USING "##.###"; pot1!
  CASE 2
    CALL POTLINC: pot1! = ADCONV!(6) * 10
    PRINT "The applied potential is now ";
    PRINT USING "##.###"; pot1!
  CASE 3
    CALL POTLDEC: pot1! = ADCONV!(6) * 10
    PRINT "The applied potential is now ";
    PRINT USING "##.###"; pot1!
  CASE 4
    PRINT "input sensitivity (either 0 or 1)";
    INPUT SENS%
    IF SENS% = 0 THEN
      DIGOUT% = DIGOUT% AND 253
      OUT &H2AD, DIGOUT%
    ELSE
      DIGOUT% = DIGOUT% OR 2
      OUT &H2AD, DIGOUT%
    END IF
  CASE 5

```



```

        DIGOUT% = DIGOUT% XOR 5
        OUT &H2AD, DIGOUT%
CASE 6
    FLAG% = 0
    CALL ICOLLECT(FLAG%): IF FLAG% = 1 THEN GOSUB 1000
CASE 7
    DIGOUT% = DIGOUT% XOR 32
    OUT &H2AD, DIGOUT%
CASE 8
    CALL PPGM
CASE 9
    DIGOUT% = DIGOUT% XOR 8
    OUT &H2AD, DIGOUT%
    START! = TIMER
RPOTWT:
    IF START! + .2 > TIMER THEN GOTO RPOTWT
    rpot1! = ADCONV1(6) * 10
    DIGOUT% = DIGOUT% XOR 8
    OUT &H2AD, DIGOUT%
    PRINT "The rest potential is ";
    PRINT USING "##.###"; rpot1!
CASE 10
    CALL IMTEST
CASE 11
    PRINT "Bye.": END
CASE 12
    CALL CONTCON
CASE ELSE
    PRINT "Please choose a menu option."
END SELECT
PRINT "type 'M' to return to menu."
DO
IF INKEY$ = "M" THEN EXIT DO
LOOP
GOTO MENUPOINT
DATA -32675,29110,25359,21608,17857,14106,10355,6604
END
1000
        'This is the fast data gathering routine
        RESTORE
        FOR D = 0 TO 7: READ EL%: SEGAR(D) = EL%: NEXT D
        PTR% = 0
        A% = 30000
        PRINT "PRESS ANY KEY TO BEGIN CONVERSIONS"
        DO
        IF INKEY$ <> "" THEN EXIT DO
        LOOP
        OUT &H2A4, 132          'Enable external start conversions
        B% = INP(&H2A6)        'Clear a/d status and overrun bits
        WHILE PTR% < 8
            DEF SEG = SEGAR(PTR%)
            I% = 0
            WHILE I% < A%
                T% = I% * 2

```

```

        IF INP(&H2A4) > 65 THEN PRINT I%; " POINT MISSED."; B =
INP(&H2A6)
        WAIT &H2A4, &H80
        LBYTE% = INP(&H2A5)
        HBYTE% = INP(&H2A6)
        POKE T%, HBYTE%
        POKE T% + 1, LBYTE%
        I% = I% + 1
    WEND
    PTR% = PTR% + 1
WEND
PRINT " THE RETRIEVAL AND STORAGE WERE SUCCESSFUL!!! "
PRINT "Writing da a to file on hard disk"
FOR n = 0 TO 7
    A$ = "c:\qbasic\tor\data\" + fl$ + CHR$(48 + n) + ".dat"
    DEF SEG = SEGAR(n)
    BSAVE A$, 0, 60000
NEXT n
OUT &H2A4, 128
RETURN

```

```

REM $STATIC
DEFSNG A-Z
SUB CINST
PRINT "This program can record up to 240000 points of data at user
specified rates."
PRINT "Data can be stored in single files up to 30000 points. A total
of 8 files"
PRINT "can be taken at any given time. The filename is user specified
and a final digit"
PRINT "is appended on the filename (from 0 to 7). Selection of sampling
rates is by "
PRINT "powers of ten only. If you want sampling at 10kHz , then you
can't choose a file"
PRINT "length or number of files. The default is 30000 points per file
and 8 files."
END SUB

```

```

DEFINT A-Z
SUB CONTCON
INPUT "CHANNEL TO CONVERT"; CH%
DO WHILE INKEY$ <> "Q"
    CONTVAL1 = ADCONV1(CH%)
    PRINT CONTVAL1
    FOR I1% = 1 TO 500: I1% = I1% ^ 2: NEXT I1%
LOOP
END SUB

```

```

DEFSNG A-Z
SUB ERRHAND (ERTYPE)
    SELECT CASE ERTYPE
        CASE 1
            BEEP: BEEP

```

```

        PRINT "OOPS, sorry I'm not that fast right now."
        PRINT "Do you wish to continue (y/n)"; : INPUT A$
        IF UCASE$(A$) = "N" THEN END
    CASE ELSE
        BEEP: BEEP: BEEP
        PRINT "UNKNOWN ERROR, execution stopped."
        CLOSE #1
        END
    END SELECT
END SUB

SUB ICOLLECT (F%)
    SHARED PTS%, fl$, FIL%
    INPUT "Do you want instructions (y/n)"; A$
    IF UCASE$(A$) = "Y" THEN CINST
    INPUT "The base filename for the data set"; fl$
    INPUT "Rate for conversion (1Hz to 10kHz)"; CONV!
    LABSETUP (CONV!): IF CONV! = 10000 THEN F% = 1: GOTO LASTLINE
    INPUT "Number of points (for less than 30000, the default)"; PTS%
    IF PTS% = 0 THEN PTS% = 30000
    IF PTS% <= 0 THEN GOTO LASTLINE
    FILNUM:
        INPUT "Number of files (1 to 8)"; TFIL%
        IF TFIL% < 1 OR TFIL% > 8 THEN BEEP: GOTO FILNUM
    PRINT "press any key to begin conversions"
    DO
        IF INKEY$ <> "" THEN EXIT DO
    LOOP
    RESTORE
    FOR D = 0 TO 7: READ ele%: segarr(D) = ele%: NEXT D
    PTR% = 0
    D = INP(&H2A6);           'clear a/d status and error bits.
    OUT &H2A4, 132           'Enable external start conversions
    WHILE PTR% < TFIL%
        I = 0
        DEF SEG = segarr(PTR%)
        WHILE I < PTS%
            T = 2 * I
            IF INP(&H2A4) > 65 THEN PRINT I; "POINT MISSED."; B = INP(&H2A6)
            WAIT &H2A4, &H80
            LBYTE% = INP(&H2A5)
            HBYTE% = INP(&H2A6)
            POKE T, HBYTE%
            POKE T + 1, LBYTE%
            I = I + 1
        WEND
        PTR% = PTR% + 1
    WEND
    PRINT "Writing data to hard disk."
    FOR D = 0 TO (TFIL% - 1)
        F$ = "C:\QBASIC\TOR\DATA\" + fl$ + CHR$(48 + D) + ".DAT"
        DEF SEG = segarr(D)
        BSAVE F$, 0, (PTS% * 2)
    
```

```

NEXT D
OUT &H2A4, 128
LASTLINE:
END SUB

SUB LABSETUP (rf!)
  ADDR = &H2A0
  OUT ADDR + 4, 128 'Disable auto-increment, load enable.
  OUT ADDR + 9, 23  'Set data ptr to Master Mode Register.
  OUT ADDR + 8, 0   'Set MMR for BCD div, 8-bit bus, comparators and
  OUT ADDR + 8, 128 'TOD disabled, low byte written first.
  OUT ADDR + 9, 5   'Set data ptr to counter 5 command reg.
  OUT ADDR + 8, 49  'Mode D, TC toggled output, BCD count down.
FREQ: PRINT rf!
  SELECT CASE rf!
    CASE 1 'User has chosen 1 Hz sampling rate.
      OUT ADDR + 8, 15 'Select F5 as counter source input.
    CASE 10 'User has chosen 10 Hz sampling rate.
      OUT ADDR + 8, 14 'Select F4 as counter source input.
    CASE 100 'You get the idea.
      OUT ADDR + 8, 13 'F3
    CASE 1000
      OUT ADDR + 8, 12 'F2
    CASE 10000
      OUT ADDR + 8, 11 'F1 1.00 MHz Oscillator.
    CASE ELSE
      PRINT "Ok bozo, try factors of 10 up to 10kHz ";
      INPUT rf
      GOTO FREQ
  END SELECT
  OUT ADDR + 8, 153 'Load counter register with decimal 99,
  OUT ADDR + 8, 0   '153 BCD = 99 decimal.
  OUT ADDR + 9, 112 'Load counter 5 and arm
  OUT ADDR + 5, 7   'Write channel number to board.
END SUB

SUB POTLDEC
  DPOT% = DPOT% - 1
  HDC% = INT(DPOT% / 256)
  LDC% = DPOT% - (HDC% * 256)
  OUT &H2A1, HDC%
  OUT &H2A0, LDC%
END SUB

SUB POTLINC
  DPOT% = DPOT% + 1
  HDC% = INT(DPOT% / 256)
  LDC% = DPOT% - (HDC% * 256)
  OUT &H2A1, HDC%
  OUT &H2A0, LDC%
END SUB

SUB POTLSET

```

```

INPUT "New potential in mV units"; POT!
DPOT% = CINT(POT! / .0481) + POFFS%
IF DPOT% < 0 THEN DPOT% = 4096 + DPOT%
HDC% = INT(DPOT% / 256)
LDC% = DPOT% - (HDC% * 256)
OUT &H2A1, HDC%
OUT &H2A0, LDC%
END SUB

```

```

DEFINT A-Z
SUB PPGM
CLS
PRINT "Welcome to the award winning pulse program (rev. 1).\"
INPUT "Base potential (w.r.t internal offset)"; BPOTL!
INPUT "Pulse potential (delta from base)"; PPOTL!
INPUT "Pulse duration (msec)"; PTIME%
INPUT "Sampling duration (sec)"; STIME!
'this section converts the potentials to digital values.
BPOT% = CINT(BPOTL! / .0495)
IF BPOT% < 0 THEN BPOT% = BPOT% + 4096
BHI% = INT(BPOT% / 256)
BLOW% = BPOT% - (BHI% * 256)
PPOT% = CINT(PPOTL! / .0495)
IF PPOT% < 0 THEN PPOT% = PPOT% + 4096
PHI% = INT(PPOT% / 256)
PLOW% = PPOT% - (PHI% * 256)
'Set potential to base value, pause 5 seconds.
OUT &H2A1, BHI%
OUT &H2A0, BLOW%
START% = TIMER + 5
DO
    IF INT(TIMER) = START% THEN EXIT DO
LOOP
LABSETUP (1000) 'configure 9513 to count at 1.00 kHz.
'set segment for storage, get pointer, and run experiment.
DEF SEG = VARSEG(addat0(0))
OFFP% = VARPTR(addat0(0))
I = 0
OUT &H2A4, 132 'start conversions
B = INP(&H2A6) 'reste a/d done flag, clear registers.
WHILE I < (STIME! * 1000)
    T = I * 2 + OFFP%
    IF INP(&H2A4) > 65 THEN PRINT I; " POINT MISSED.": B = INP(&H2A6)
    WAIT &H2A4, &H80
    LBYTE% = INP(&H2A5)
    HBYTE% = INP(&H2A6)
    POKE T, HBYTE%
    POKE T + 1, LBYTE%
    IF I = 20 THEN
        OUT &H2A1, PHI%
        OUT &H2A0, PLOW%
    ELSEIF I = (20 + PTIME%) THEN
        OUT &H2A1, BHI%

```

```

        OUT &H2A0, BLOW%
    END IF
    I = I + 1
WEND
OUT &H2A4, 128
PRINT "DONE!"
END SUB

```

Code for IMTEST module of WRKSPCE.BAS:

```

'IMTEST MODULE LEVEL CODE
DECLARE SUB STWAIT ()
DECLARE FUNCTION GETVAL! (SS%, CH%)
DECLARE SUB CHGFREQ ()
DECLARE FUNCTION LOG10! (X!)
DECLARE FUNCTION DETSENS! ()
' Common GPIB status variables

COMMON SHARED IBSTA%, IBERR%, IBCNT%

' GPIB Subroutine Declarations

DECLARE SUB IBRD (BD%, RD%)
DECLARE SUB IBRSP (BD%, SPR%)
DECLARE SUB IBWRT (BD%, WRT%)

' GPIB Function Declarations

DECLARE FUNCTION ILFIND% (BDNAME$)

DIM SHARED XARR(500) AS SINGLE, YARR(500) AS SINGLE, MARR(500) AS SINGLE
DIM SHARED TARR(500) AS SINGLE, FARR(500) AS SINGLE
DIM SHARED R$(10), LOCKIN%, LSTEP!, CT%, FREQ
CONST PI = 3.141593
TYPE CURVETYPE
    XVL AS SINGLE
    YVL AS SINGLE
    MAG AS SINGLE
    THE AS SINGLE
    FREQ AS SINGLE
END TYPE
DIM SHARED CURVERECORD AS CURVETYPE

SUB CHGFREQ
N2% = -INT(LOG10!(FREQ / 10000))
N1% = (FREQ / (10 ^ (2 - N2%)))
LCD$ = "J " + LTRIM$(RTRIM$(STR$(N1%))) + CHR$(32) +
LTRIM$(RTRIM$(STR$(N2%)))
CALL IBWRT(LOCKIN%, LCD$)
END SUB

FUNCTION DETSENS!

```

```

LCD$ = "S"
CALL IBWRT(LOCKIN%, LCD$)
RD$ = SPACE$(10)
CALL IBRD(LOCKIN%, RD$)
SENS% = VAL(RD$)
T1% = SENS% + 1 - (INT(SENS% / 3) * 3)
IF T1% = 1 THEN T1% = 5
IF T1% = 3 THEN T1% = 1
DETSENS! = (10 ^ (-INT(SENS% / 3))) * T1%
END FUNCTION

```

```

FUNCTION GETVAL! (SS%, CH%)
SUM! = 0
FOR I = 1 TO SS%
    INIT = TIMER
WAITMORE:      'INSTALL 200ms WAIT LOOP TO PREVENT FREEZ-UPS
    IF INIT + .2 > TIMER THEN GOTO WAITMORE
    A$ = "Q" + LTRIM$(STR$(CH%))
    CALL IBWRT(LOCKIN%, A$)
    RD$ = SPACE$(10)
    CALL IBRD(LOCKIN%, RD$)
    SUM! = (VAL(RD$) / 2000) + SUM!
NEXT I
GETVAL! = SUM! / SS%
END FUNCTION

```

```

SUB IMTEST
DEV$ = "PAR5208"
LOCKIN% = ILFIND%(DEV$)
'USER INITIALIZATION
PRINT
PRINT
PRINT "This is an ac impedance measurement program"
INPUT "Number of points to be averaged at starting frequency"; SAM%
INPUT "Number of points per decade"; DIV%
LSTEP! = 1 / DIV%
INPUT "Starting frequency (in Hz)"; SFREQ!
INPUT "Ending frequency (in Hz)"; EFREQ!
CLS
LCD$ = "A1 1"
CALL IBWRT(LOCKIN%, LCD$)
CALL STWAIT
CT% = 0
FREQ = SFREQ!
SAM% = SAM% * SFREQ!
N2% = -INT(LOG10!(FREQ / 10000))
N1% = (FREQ / (10 ^ (2 - N2%)))
LCD$ = "J " + LTRIM$(RTRIM$(STR$(N1%))) + CHR$(32) +
LTRIM$(RTRIM$(STR$(N2%)))
CALL IBWRT(LOCKIN%, LCD$)
DO
    CT% = CT% + 1
    CALL STWAIT

```

```

SAMPS% = INT(SAM% / FREQ + 1)
' READ VALUES FROM LOCKIN, BEGINNING WITH X CHANNEL
CHAN% = 1
XVL = GETVAL!(SAMPS%, CHAN%) * DETSENS!
CHAN% = 2
YVL = GETVAL!(SAMPS%, CHAN%) * DETSENS!
' INCREMENT FREQUENCY
CURFREQ! = FREQ
FREQ = 10 ^ (LOG10!(FREQ) + LSTEP!)
CALL CHGFREQ
' CONVERT X AND Y VALUES TO MAGNITUDE AND ANGLE
MARR(CT%) = SQR((XVL ^ 2) + (YVL ^ 2)) * 1000
IF YVL < 0 AND XVL < 0 THEN
    CORR = -PI
ELSEIF YVL > 0 AND XVL < 0 THEN
    CORR = PI
ELSE
    CORR = 0!
END IF
TARR(CT%) = (ATN(YVL / XVL) + CORR) * 180 / PI
FARR(CT%) = CURFREQ!
XARR(CT%) = XVL
YARR(CT%) = YVL
    LOOP WHILE CURFREQ! < EFREQ!
' Finished with scan, provide options print, save (file), or quit.
DONE:
INPUT "Impedance scan finished, continue (P,F,Q)"; A$
IF UCASE$(A$) = "Q" THEN
    GOTO SUBENDER
ELSEIF UCASE$(A$) = "P" THEN
    FOR I = 1 TO CT%
        LPRINT USING "#####.##"; FARR(I), MARR(I), TARR(I)
    NEXT I
ELSEIF UCASE$(A$) = "F" THEN
    INPUT "Filename (omit .dat)"; IFIL$
    IFNAM$ = "\qbasic\tor\data\" + IFIL$ + ".DAT"
    OPEN IFNAM$ FOR RANDOM AS #255 LEN = LEN(CURVERECORD)
    FOR I = 1 TO CT%
        CURVERECORD.XVL = XARR(I)
        CURVERECORD.YVL = YARR(I)
        CURVERECORD.MAG = MARR(I)
        CURVERECORD.THE = TARR(I)
        CURVERECORD.FREQ = FARR(I)
        PUT #255, I, CURVERECORD
    NEXT I
    CLOSE #255
    PRINT "Data set saved."
    PRINT
ELSE
    GOTO DONE
END IF
GOTO DONE
SUBENDER:

```


END SUB

```
FUNCTION LOG10! (X!)
LOG10! = LOG(X!) / LOG(10#)
END FUNCTION
```

```
SUB STWAIT
DO
  CALL IBRSP(LOCKIN%, ST%)
  IF ST% AND 1 THEN GOTO SETTLE
  LOOP
SETTLE:
  'WAIT 1.5 SECONDS
  INIT = TIMER
WTLOOP:
  IF INIT + 1.5 > TIMER THEN GOTO WTLOOP
DO
  CALL IBRSP(LOCKIN%, ST%)
  IF ST% AND 16 THEN GOTO WTLOOP
  IF ST% AND 32 THEN EXIT DO
  LOOP
END SUB
```

FILEPLOT.BAS source code:

```
DECLARE FUNCTION AMX! (ARR!())
DECLARE FUNCTION AMN! (ARR!())
DECLARE FUNCTION BLAH! (X!)
DECLARE SUB MDLCRV (RATE!, L&, R&)
DECLARE FUNCTION AVGEXP! (L&, R&)
DECLARE FUNCTION STEPEXP! (DM&)
DECLARE FUNCTION FILEINT# (L&, R&, CHK)
DECLARE FUNCTION VARSTR$ (IN!)
DECLARE FUNCTION ILFIND$ (BDNAME$)
COMMON SHARED IBSTA%, IBERR%, IBCNT%
DECLARE SUB IBWRT (BD%, WRT$)
DECLARE SUB PLOTDATA ()
DECLARE SUB SKANSKRN ()
DECLARE SUB SCREENPLOT ()
DECLARE SUB SHIFTRIGHT ()
DECLARE SUB SHIFLEFT ()
DECLARE SUB XYPLOT (XARR!(), YARR!())
REM $DYNAMIC
DIM SHARED ADDAT0(30000) AS INTEGER
DIM SHARED ADDAT1(30000) AS INTEGER
DIM SHARED ADDAT2(30000) AS INTEGER
DIM SHARED IMAGE(1 TO 25) AS INTEGER
DIM SHARED PLOTAR(599) AS INTEGER, PXMAX!, PXMIN!, PYMAX!, PYMIN!,
SDIV!, SECW!
DIM SHARED FPTS%, AMAX%, AMIN%, LP&, HP&, PPP&, PLO%, WRT$(255), F%,
CONFLAG%
```

```

DIM SHARED MDLAR(600) AS SINGLE
CONST YOFFS% = 147
CONST YMULT% = 127
CONST PI = 3.14159265#
DIM FSPEC$(12)
DIM SHARED XARR!(15000), YARR!(15000)
MAINLOAD:
INPUT "Number of files to load (3 or less)"; NFIL%
INPUT "Sensitivity scale (0 or 1)"; S%
IF S% = 1 THEN
    SDIV! = 40.96
ELSE
    SDIV! = 4.096
END IF
INPUT "file length (bytes-7)/2 "; FPTS%
FOR I = 0 TO (NFIL% - 1)
INPUT "please enter the full filename"; FSPEC$: F$ = "\qbasic\tor\data\"
+ FSPEC$
SELECT CASE I
    CASE 0
        REDIM ADDAT0(FPTS% - 1) AS INTEGER
        DEF SEG = VARSEG(ADDAT0(0))
        BLOAD F$, VARPTR(ADDAT0(0))
    CASE 1
        REDIM ADDAT1(FPTS% - 1) AS INTEGER
        DEF SEG = VARSEG(ADDAT1(1))
        BLOAD F$, VARPTR(ADDAT1(1))
    CASE 2
        REDIM ADDAT2(FPTS% - 1) AS INTEGER
        DEF SEG = VARSEG(ADDAT2(2))
        BLOAD F$, VARPTR(ADDAT2(2))
END SELECT
NEXT I
MENU:
PRINT "OPTIONS:"
PRINT "    1=VIEW DATA ON SCREEN"
PRINT "    2=FILE INTEGRATE"
PRINT "    3=APPEND TO LEFT(EARLIER TIME DATA)"
PRINT "    4=APPEND TO RIGHT(LATER TIME DATA)"
PRINT "    5=EXIT"
INPUT "    YOUR CHOICE"; CH%
SELECT CASE CH%
    CASE 1
        CALL SCREENPLOT
    CASE 2
        INPUT "WHICH FILE"; F%
        PRINT USING "####.###"; FILEINT#(0, 29999, 0)
    CASE 3
        CALL SHIFLEFT
    CASE 4
        CALL SHIFTRIGHT
    CASE 5
        GOTO CLOSER

```

```

        CASE ELSE
        BEEP: GOTO MENU
        END SELECT

GOTO MENU
CLOSER:
CLS : PRINT "BYE."
END
1000 SCREEN 0: GOTO CLOSER
2000 PRINT "BURP IN SCAN PROGRAM": CALL SKANSKRN: CALL SCREENPLOT: GOTO
MENU

REM $STATIC
FUNCTION AMN! (ARR!())
DEFINT A-Z
B = 0
T = 600
MIN! = ARR!(B)
FOR I = (B + 1) TO T
    IF ARR!(I) < MIN! THEN MIN! = ARR!(I)
NEXT I
AMN! = MIN!
END FUNCTION

DEFSNG A-Z
FUNCTION AMX! (ARR!())
DEFINT A-Z
B = 0
T = 600
MAX! = ARR!(B)
FOR I = (B + 1) TO T
    IF ARR!(I) > MAX! THEN MAX! = ARR!(I)
NEXT I
AMX! = MAX!
END FUNCTION

DEFSNG A-Z
FUNCTION AVGEXP! (L&, R&)
RA! = .00381
RA2! = RA! ^ 2
AREA# = FILEINT#(L&, R&, 1) * 4.50045E-06
'GET LOWER BOUND FOR THETA
THETA! = (12 * AREA# / RA2!) ^ .333333#
'BEGIN LOGARITHMIC ITERATION
STPSIZ = .1
THETA! = THETA! - STPSIZ
ITERATE:
DO
    THETA! = THETA! + STPSIZ
    K# = RA2! * (THETA! - SIN(THETA!)) / 2
    IF K# > AREA# THEN
        THETA! = THETA! - STPSIZ
        STPSIZ = STPSIZ / 10
        IF STPSIZ < .0000001 THEN EXIT DO

```

```

    END IF
LOOP
SECW! = RA! * (1 - COS(THETA! / 2))
PRINT SECW!,
AVGEXP! = SQR(SECW! * 2 * RA!) / ((R& - L&) * .001)
END FUNCTION

FUNCTION BLAH (X!)
BLAH = PI / 2 - ATN(X! / SQR(1! - (X! ^ 2)))
END FUNCTION

FUNCTION FILEINT# (L&, R&, CHK) STATIC
'TRAPEZOID RULE DATA POINT INTEGRATION
SELECT CASE F%
CASE 1
DEF SEG = VARSEG(ADDAT0(0))
OFFS% = VARPTR(ADDAT0(L&))
CASE 2
DEF SEG = VARSEG(ADDAT1(0))
OFFS% = VARPTR(ADDAT1(L&))
CASE 3
DEF SEG = VARSEG(ADDAT2(0))
OFFS% = VARPTR(ADDAT2(L&))
END SELECT
RUNINT# = 0
FOR I = 0 TO R& - L&
T& = I * 2 + OFFS%
HBYTE& = PEEK(T&)
LBYTE& = PEEK(T& + 1)
ADDAT& = ((HBYTE& * 256&) + LBYTE&)
IF ADDAT& > 32767 THEN ADDAT& = ADDAT& - 65536
ADDAT# = ADDAT& / SDIV!
IF I = 0 THEN
LMIN = ADDAT#
ADDAT# = ADDAT# / 2
ELSEIF I = R& - L& THEN
RMIN = ADDAT#
ADDAT# = ADDAT# / 2
END IF
RUNINT# = RUNINT# + ADDAT# * .001
NEXT I
IF CHK = 0 THEN FILEINT# = RUNINT#: GOTO CLOSER3
'SUBTRACT OUT BACKGROUND BY FITTING A LINE THROUGH BASELINE
BCUR = (RMIN + LMIN) / 2
BQ = BCUR * (R& - L&) * .001
FILEINT# = RUNINT# - BQ
CLOSER3:
END FUNCTION

SUB MDLCRV (RATE!, L&, R&)
REDIM MDLAR(600) AS SINGLE
Q! = AVGEXP!(L&, R&)
H! = SECW!

```

```

RA! = .00381
OFFSET:
INPUT "offset in y direction"; Y1
IF Y1 > H! THEN BEEP: PRINT "OFFSET MUST BE LESS THAN "; H!; ".": GOTO
OFFSET
X1 = -SQR((2 * Y1 * RA!) - Y1 ^ 2)
ALPHA = BLAH((RA! - Y1) / RA!)
SLOPE = TAN(ALPHA)
INTCPT = (H! - Y1) / COS(ALPHA)
INTCPT2 = INTCPT ^ 2
QT! = (SLOPE ^ 2 + 1)
CP! = SQR(2 * RA! * H! - H! ^ 2)
STP2! = SQR((CP! + X1) ^ 2 + H! ^ 2)
SP% = L% - LP%
FOR I = L% TO R%
  TM! = I - L%
  RADIUS! = RATE! * TM! / 1000
  RATIO1! = (RADIUS! / (2 * RA!))
  IF RADIUS! < H! - Y1 THEN
    MDLAR(TM! + SP%) = RADIUS! * RATE! * .0004444 * BLAH(RATIO1!)
  ELSEIF RADIUS! > H! - Y1 AND RADIUS! < STP2! THEN
    YR! = (INTCPT + SQR(INTCPT2 + QT! * ((SLOPE * RADIUS!) ^ 2 -
INTCPT2))) / QT!
    RATIO2! = (YR! / RADIUS!)
    MDLAR(TM! + SP%) = RADIUS! * RATE! * .0004444# * (BLAH(RATIO1!) -
BLAH(RATIO2!)) - ALPHA)
  ELSEIF RADIUS! > STP2! THEN
    YR! = (INTCPT + SQR(INTCPT2 + QT! * ((SLOPE * RADIUS!) ^ 2 -
INTCPT2))) / QT!
    RATIO2! = (YR! / RADIUS!)
    MDLAR(TM! + SP%) = RADIUS! * RATE! * .0002222 * (BLAH(RATIO1!) -
BLAH(RATIO2!))
    IF MDLAR(TM! + SP%) < 0 THEN MDLAR(TM! + SP%) = 0
  END IF
NEXT I
PYI! = AMN!(MDLAR())
PYA! = AMX!(MDLAR())
PRINT PYI!, PYA!
PSET (0, 167)
FOR I = 40 TO 639
  PY% = YOFFS% - ((4.096E+10 * MDLAR(I - 40)) - AMIN%) / (AMAX% -
AMIN%) * YMULT%
  LINE -(I, PY%)
NEXT I
END SUB

SUB PLOTDATA
SCREEN 0
DEV$ = "PLOTTER"
PLO% = ILFIND(DEV$)
X$ = "TIME(msec)"
Y$ = "CURRENT (nA)"
PYMAX! = AMAX% / SDIV!

```

```

    PYMIN! = AMIN% / SDIV!
    PXMIN! = LP%
    PXMAX! = HP% - 1
    WRT$ = "IN;VS5;SP1;IP1280,1280,10250,7796;SC0,10000,0,10000;": CALL
IBWRT(PLO%, WRT$)
    XTP! = -1000: XLP! = -360: YTP! = -1300: YLP! = -900
AXLABEL:
'This section gets numeric labels for the axes.
'There three labels for the x-axis and four labels
'for the y-axis.
    LX1! = (PXMIN! * 100) / 100
    LX2! = ((PXMAX! - PXMIN!) * 50) / 100 + LX1!
    LX3! = (PXMAX! * 100) / 100
    LY1! = (PYMIN! * 100) / 100
    LY2! = ((PYMAX! - PYMIN!) * 30) / 100 + LY1!
    LY3! = ((PYMAX! - PYMIN!) * 70) / 100 + LY1!
    LY4! = (PYMAX! * 100) / 100
'Draw axes with plotter, using pen 1.

    WRT$ = "PA0,0;PD;XT;": CALL IBWRT(PLO%, WRT$)
    WRT$ = "PR1000,0;XT;":
    FOR I = 1 TO 10
        CALL IBWRT(PLO%, WRT$)
    NEXT I
    WRT$ = "PU;PA0,0;PD;YT;": CALL IBWRT(PLO%, WRT$)
    WRT$ = "PR0,1000;YT;":
    FOR I = 1 TO 10
        CALL IBWRT(PLO%, WRT$)
    NEXT I
'Label x-axis with title and values
    WRT$ = "SP2;PU;PA4250," + VARSTR$(XTP!) + ";LB" + X$ + CHR$(3):
CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA0," + VARSTR$(XLP!) + ";LB" + VARSTR$(LX1!) + CHR$(3):
CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA4500," + VARSTR$(XLP!) + ";LB" + VARSTR$(LX2!) +
CHR$(3): CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA9500," + VARSTR$(XLP!) + ";LB" + VARSTR$(LX3!) +
CHR$(3): CALL IBWRT(PLO%, WRT$)
'Label y-axis with title and values
    WRT$ = "PA" + VARSTR$(YTP!) + ",3700;DI0,1;LB" + Y$ + CHR$(3):
CALL IBWRT(PLO%, WRT$)
    WRT$ = "DI;PA" + VARSTR$(YLP!) + ",0;LB" + VARSTR$(LY1!) +
CHR$(3): CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA" + VARSTR$(YLP!) + ",3000;LB" + VARSTR$(LY2!) +
CHR$(3): CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA" + VARSTR$(YLP!) + ",7000;LB" + VARSTR$(LY3!) +
CHR$(3): CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA" + VARSTR$(YLP!) + ",10000;LB" + VARSTR$(LY4!) +
CHR$(3): CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA0,0;": CALL IBWRT(PLO%, WRT$)
SELECT CASE F%
CASE 1 'PLOTING ADDATO
    DEF SEG = VARSEG(ADDAT0(0))

```

```

        OFFS% = VARPTR(ADDAT0(0))
CASE 2 'PLOTING ADDAT1
    DEF SEG = VARSEG(ADDAT1(0))
    OFFS% = VARPTR(ADDAT1(0))
CASE 3 'PLOTING ADDAT2
    DEF SEG = VARSEG(ADDAT2(0))
    OFFS% = VARPTR(ADDAT2(0))
END SELECT
    INCR% = 1
    IF HP% - LP% - 1 > 15000 THEN INCR% = 2
FOR I = LP% TO HP% - 1
    T% = (I) * 2 * INCR% + OFFS%
    HBYTE% = PEEK(T%)
    LBYTE% = PEEK(T% + 1)
    ADDAT% = (HBYTE% * 256%) + LBYTE%
    IF ADDAT% > 32767 THEN ADDAT% = ADLAT% - 65536
    CUR% = ADDAT% / SDIV%
    YARR%(I - LP%) = CUR%
    XARR%(I - LP%) = I - LP%
NEXT I

```

```

CALL XYPLOT(XARR%(), YARR%())
SCREEN 2
LINE (100, 100)-(120, 100)
LINE (110, 95)-(110, 105)
GET (100, 95)-(120, 105), IMAGE
PUT (100, 95), IMAGE, XOR
VIEW SCREEN (40, 0)-(639, 167), , 1
VIEW PRINT 23 TO 24
END SUB

```

```

SUB SCREENPLOT
SCREEN 2
LINE (100, 100)-(120, 100)
LINE (110, 95)-(110, 105)
GET (100, 95)-(120, 105), IMAGE
PUT (100, 95), IMAGE, XOR
VIEW SCREEN (40, 0)-(639, 167), , 1
VIEW PRINT 23 TO 24
ARCHOOSE:
INPUT "PLOT FILE (999) TO EXIT"; F%
SELE:
SELECT CASE F%

```

```

    CASE 1 'PLOTING ADDAT0
        DEF SEG = VARSEG(ADDAT0(0))
        OFFS% = VARPTR(ADDAT0(0))
    CASE 2 'PLOTING ADDAT1
        DEF SEG = VARSEG(ADDAT1(0))
        OFFS% = VARPTR(ADDAT1(0))
    CASE 3 'PLOTING ADDAT2
        DEF SEG = VARSEG(ADDAT2(0))
        OFFS% = VARPTR(ADDAT2(0))
CASE 999
    GOTO CLOSER1

```

```

CASE ELSE
    INPUT "SELECT FILE (1-3) OR 999 TO EXIT"; F$: GOTO SELE
END SELECT
INPUT "POINTS PER PIXEL"; PPP&
INPUT "STARTING POINT"; SP&
LP& = SP& - 1
HP& = LP& + (PPP& * 600)
IF HP& > FPTS% - 1 THEN HP& = FPTS% - 1
CONVERT:
AMAX% = 1
AMIN% = 5000
FOR I = LP& TO (HP& - 1) STEP PPP&
    T& = 2 * I + OFFS&
    HBYTE& = PEEK(T&)
    LBYTE& = PEEK(T& + 1)
    ADDAT& = (HBYTE& * 256) + LBYTE&
    IF ADDAT& > 32767 THEN ADDAT& = ADDAT& - 65536
    ADC% = CINT(ADDAT&)
    PLOTAR((I - LP&) / PPP&) = ADC%
    IF ADC% > AMAX% THEN AMAX% = ADC% + 1
    IF ADC% < AMIN% THEN AMIN% = ADC%
NEXT I
CHOICE:
'PLOT DATA ARRAY ON SCREEN
FOR I = 40 TO 639
    PY& = YOFFS% - (PLOTAR(I - 40) - AMIN%) / (AMAX% - AMIN%) *
YMULT%
    PSET (I, PY&)
NEXT I
INPUT "CONTINUE SERIES, SCAN OR EXIT (Y,S,E,P)"; A$
IF UCASE$(A$) = "Y" THEN
    LP& = HP&
    HP& = HP& + (PPP& * 600)
    CLS 1: GOTO CONVERT
ELSEIF UCASE$(A$) = "S" THEN
    CALL SKANSKRN: GOTO CHOICE
ELSEIF UCASE$(A$) = "P" THEN
    CALL PLOTDATA: GOTO CHOICE
END IF
CLS 1
GOTO ARCHOOSE
CLOSER1:
SCREEN 0: CLS
END SUB

SUB SHIFTLTLEFT
FOR I = 0 TO FPTS% - 1
    ADDAT2(I) = ADDAT1(I)
    ADDAT1(I) = ADDAT0(I)
NEXT I
INPUT "please enter the full filename"; FSPEC$: F$ = "\qbasic\tor\data\"
+ FSPEC$
INPUT "file length (bytes-7)/2 "; FPTS%

```



```

REDIM ADDAT0(FPTS% - 1) AS INTEGER
DEF SEG = VARSEG(ADDAT0(0))
BLOAD F$, VARPTR(ADDAT0(0))
END SUB

SUB SHIFTRIGHT
FOR I = 0 TO FPTS% - 1
    ADDAT0(I) = ADDAT1(I)
    ADDAT1(I) = ADDAT2(I)
NEXT I
INPUT "please enter the full filename"; FSPEC$: F$ = "\qbasic\tor\data\"
+ FSPEC$
INPUT "file length (bytes-7)/2 "; FPTS%
REDIM ADDAT2(FPTS% - 1) AS INTEGER
DEF SEG = VARSEG(ADDAT2(0))
BLOAD F$, VARPTR(ADDAT2(0))
END SUB

SUB SKANSKRN
SELECTX:
PRINT "MIN. FILE POINT "; LP&; " MAX FILE POINT "; HP&
INPUT "STARTING X POINT"; PX&
IF PX& < LP& OR PX& > HP& THEN BEEP: GOTO SELECTX
ON ERROR GOTO 2000
' MOTION LOOP
IMAGPUT:
SPX% = (PX% - LP%) / PPP% + 40
SPY% = YOFFS% - (PLOTAR(SPX% - 40) - AMIN%) / (AMAX% - AMIN%) * YMULT%
PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
DO
A$ = INKEY$
SELECT CASE A$
CASE IS = "P"
PRINT PX&, (PLOTAR(SPX% - 40)) / SDIV!
CASE IS = "H"
IF SPX% > 60 THEN
PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
SPX% = SPX% - 10
EXIT DO
END IF
CASE IS = "L"
IF SPX% < 629 THEN
PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
SPX% = SPX% + 10
EXIT DO
END IF
CASE IS = "Q"
GOTO CLOSER2
CASE IS = "J"
PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
PX% = PX% - 1: GOTO IMAGPUT
CASE IS = "K"
PUT (SPX% - 10, SPY% - 5), IMAGE, XOR

```

```

    PX& = PX& + 1: GOTO IMAGPUT
CASE IS = "1"
    LMARK& = PX&: PRINT LMARK&
CASE IS = "2"
    RMARK& = PX&: PRINT RMARK&
CASE IS = "I"
    IF RMARK& <= LMARK& THEN
        PRINT "ERROR IN MARKING"
    ELSE PRINT USING "####.###"; FILEINT#(LMARK&, RMARK&, 1)
    END IF
CASE IS = "D"
    PRINT STEPEXP!(LMARK&)
CASE IS = "S"
    IF RMARK& <= LMARK& THEN
        PRINT "ERROR IN MARKING"
    ELSE PRINT AVGEXP!(LMARK&, RMARK&)
    END IF
CASE IS = "M"
    INPUT "RATE OF EXPANSION"; RATE!
    CALL MDLCRV(RATE!, LMARK&, RMARK&)
CASE ELSE
END SELECT
LOOP
PX& = ((SPX& - 40) * PPP&) + LP&
GOTO IMAGPUT
CLOSER2:
CLS
END SUB

FUNCTION STEPEXP! (DM&)
'THIS IS A ROUTINE WHICH FITS A USER SET NUMBER OF POINTS AND CALCULATES
'THE STEP EXPANSION COEFF. BY  $di/dt = \pi * q * k^2$ .
INPUT "Number of points"; N%: ORIG& = DM& - N% \ 2
SELECT CASE F%
CASE 1
    DEF SEG = VARSEG(ADDAT0(0))
    OFFS% = VARPTR(ADDAT0(ORIG&))
CASE 2
    DEF SEG = VARSEG(ADDAT1(0))
    OFFS% = VARPTR(ADDAT1(ORIG&))
CASE 3
    DEF SEG = VARSEG(ADDAT2(0))
    OFFS% = VARPTR(ADDAT2(ORIG&))
END SELECT
SX! = 0: SY! = 0: SXY! = 0: SXX! = 0
FOR C = 0 TO (N% - 1)
    T& = C * 2 + OFFS%
    HBYTE& = PEEK(T&)
    LBYTE& = PEEK(T& + 1)
    ADDAT& = ((HBYTE& * 256&) + LBYTE&)
    IF ADDAT& > 32767 THEN ADDAT& = ADDAT& - 65536
    ADDT! = ADDAT& / SDIV!
    SX! = SX! + C

```

```

    SY! = SY! + ADDT!
    SKY! = SKY! + ADDT! * C
    SXX! = SXX! + (C ^ 2)
NEXT C
'EXTRACT LEAST SQUARES SLOPE, GET K USING Ag(111) DENSITY
SLOPE! = (N% * SKY! - SY! * SX!) / (N% * SXX! - SX! * SX!)
STEPEXP! = SQR(SLOPE! / 698.062)
END FUNCTION

FUNCTION VARSTR$ (IN!)
D = 1
XP$ = STR$(IN!)
VTR$ = LTRIM$(RTRIM$(XP$))
FOR I = 1 TO LEN(VTR$)
    IF MID$(VTR$, I, 1) = "." THEN VARSTR$ = MID$(VTR$, 1, I + 2): D
= -1
    IF I = LEN(VTR$) AND D = 1 THEN VARSTR$ = VTR$
NEXT I
    IF ABS(IN!) < .1 THEN VARSTR$ = "0"
END FUNCTION

SUB XYPLOT (XARR!(), YARR!())
WRT$ = "SP3;VS5;PU;": CALL IBWRT(PLO%, WRT$)
DIVIDER% = HP% - LP% - 1
FOR I = 0 TO DIVIDER%
    XP! = (XARR!(I) / DIVIDER%) * 10000
    YP! = (YARR!(I) - PYMIN!) / (PYMAX! - PYMIN!) * 10000
    WRT$ = "PA" + VARSTR$(XP!) + "," + VARSTR$(YP!) + ";PD;"
    CALL IBWRT(PLO%, WRT$)
NEXT I
WRT$ = "PA;SP0;PA0,0;IN;": CALL IBWRT(PLO%, WRT$)
END SUB

```

LUNFIT.BAS source code:

```

DECLARE SUB MODSPLOT (L%)
DECLARE SUB LUNSIM (L%, R%, M%, MDLCRV(), MDLEND%)
DECLARE SUB SCREENINIT ()
DECLARE FUNCTION AMX! (ARR!())
DECLARE FUNCTION AMN! (ARR!())
DECLARE FUNCTION LSTEXP! (L%, M%)
DECLARE FUNCTION FILEINT# (L%, R%, CHK)
DECLARE FUNCTION VARSTR$ (IN!)
DECLARE FUNCTION ILFIND% (BDNAME$)
COMMON SHARED IBSTA%, IBERR%, IBCNT%
DECLARE SUB IBWRT (BD%, WRT$)
DECLARE SUB PLOTDATA ()
DECLARE SUB SKANSKRN ()
DECLARE SUB SCREENPLOT ()
DECLARE SUB SHIFTRIGHT ()
DECLARE SUB SHIFLEFT ()
DECLARE SUB XYPLOT (XARR!(), YARR!(), IFUL%)

```

```

REM $DYNAMIC
DIM SHARED ADDAT0(30000) AS INTEGER
DIM SHARED IMAGE(1 TO 25) AS INTEGER
DIM SHARED PLOTAR(599) AS INTEGER, PXMAX!, PXMIN!, PYMAX!, PYMIN!, SDIV!
DIM SHARED SECW!, RP%, XARR!(15000), YARR!(15000)
DIM SHARED FPT$%, AMAX%, AMIN%, LP%, HP%, PPP%, PLO%, WRT$(255), F%,
CONFLAG%
DIM SHARED MDLCRV(6000) AS SINGLE, PLTMDL(6000) AS SINGLE, MDFLAG%,
MDLEND%
CONST YOFFS% = 150
CONST YMULT% = 120
CONST PI = 3.14159265#
RP% = 0
DIM FSPEC$(12)
MAINLOAD:
INPUT "Sensitivity scale (0 or 1)"; S%
IF S% = 1 THEN
    SDIV! = 40.96
ELSE
    SDIV! = 4.096
END IF
INPUT "file length (bytes-7)/2 "; FPT$%
INPUT "please enter the full filename"; FSPEC$
F$ = "c:\qbasic\tor\data\" + FSPEC$
REDIM ADDAT0(FPT$% - 1) AS INTEGER
DEF SEG = VARSEG(ADDAT0(0))
BLOAD F$, VARPTR(ADDAT0(0))

MENU:
PRINT "OPTIONS:"
PRINT "      1=VIEW DATA ON SCREEN"
PRINT "      2=FILE INTEGRATE"
PRINT "      3=LOAD FILE"
PRINT "      4=EXIT"
INPUT "      YOUR CHOICE"; CH%
SELECT CASE CH%
    CASE 1
        CALL SCREENPLOT
    CASE 2
        PRINT USING "####.###"; FILEINT$(0, 29999, 0)
    CASE 3
        GOTO MAINLOAD
    CASE 4
        GOTO CLOSER
    CASE ELSE
        BEEP: GOTO MENU
END SELECT

GOTO MENU
CLOSER:
CLS : PRINT "BYE."
END
1000 SCREEN 0: GOTO CLOSER
2000 PRINT "BURP IN SCAN PROGRAM": CALL SKANSKRN: CALL SCREENPLOT: GOTO
MENU

```

```

REM $STATIC
FUNCTION AMN! (ARR!())
DEFINT A-Z
B = 0
T = 600
MIN! = ARR!(B)
FOR I = (B + 1) TO T
    IF ARR!(I) < MIN! THEN MIN! = ARR!(I)
NEXT I
AMN! = MIN!
END FUNCTION

DEFSNG A-Z
FUNCTION AMX! (ARR!())
DEFINT A-Z
B = 0
T = 600
MAX! = ARR!(B)
FOR I = (B + 1) TO T
    IF ARR!(I) > MAX! THEN MAX! = ARR!(I)
NEXT I
AMX! = MAX!
END FUNCTION

DEFSNG A-Z
FUNCTION FILEINT# (L&, R&, CHK) STATIC
'TRAPEZOID RULE DATA POINT INTEGRATION
DEF SEG = VARSEG(ADDAT0(0))
OFFS% = VARPTR(ADDAT0(L&))
RUNINT# = 0
FOR I = 0 TO R& - L&
    T& = I * 2 + OFFS%
    HBYTE& = PEEK(T&)
    LBYTE& = PEEK(T& + 1)
    ADDAT& = ((HBYTE& * 256&) + LBYTE&)
    IF ADDAT& > 32767 THEN ADDAT& = ADDAT& - 65536
    ADDAT# = ADDAT& / SDIV!
    IF I = 0 THEN
        LMIN = ADDAT#
        ADDAT# = ADDAT# / 2
    ELSEIF I = R& - L& THEN
        RMIN = ADDAT#
        ADDAT# = ADDAT# / 2
    END IF
    RUNINT# = RUNINT# + ADDAT# * .001
NEXT I
IF CHK = 0 THEN FILEINT# = RUNINT#: GOTO CLOSER3
'SUBTRACT OUT BACKGROUND BY FITTING A LINE THROUGH BASELINE
BCUR = (RMIN + LMIN) / 2
BQ = BCUR * (R& - L&) * .001
FILEINT# = RUNINT# - BQ
CLOSER3:

```

END FUNCTION

```
FUNCTION LSTEXP! (L&, M&)  
'THIS IS A ROUTINE WHICH FITS A USER SET NUMBER OF POINTS AND CALCULATES  
'THE STEP EXPANSION COEFF. BY  $di/dt = \pi * q * k^2$ .  
DEF SEG = VARSEG(ADDAT0(0))  
OFFS% = VARPTR(ADDAT0(L&))  
SX! = 0: SY! = 0: SXY! = 0: SXX! = 0  
N% = 0  
FOR C = 0 TO (M& - L& - 1)  
  T% = C * 2 + OFFS%  
  HBYTE% = PEEK(T%)  
  LBYTE% = PEEK(T% + 1)  
  ADDAT% = ((HBYTE% * 256%) + LBYTE%)  
  IF ADDAT% > 32767 THEN ADDAT% = ADDAT% - 65536  
  ADDT! = ADDAT% / SDIV!  
  SX! = SX! + C  
  SY! = SY! + ADDT!  
  SXY! = SXY! + ADDT! * C  
  SXX! = SXX! + (C ^ 2)  
  N% = N% + 1  
NEXT C  
'EXTRACT LEAST SQUARES SLOPE, GET K USING Ag(111) DENSITY  
SLOPE! = (N% * SXY! - SY! * SX!) / (N% * SXX! - SX! * SX!)  
LSTEXP! = SQR(SLOPE! / 698.062)  
END FUNCTION
```

```
SUB MODSPLOT (L&)  
'THIS SUBROUTINE TAKES THE MODEL ARRAY FORM LUNSIM AND PUTS IT INTO  
'THE SCREEN BASED PLOTTING ARRAY "PLTMDL"  
STARTPT% = (((L& - LP&) \ PPP&) * 10)  
C = 0  
FOR I = STARTPT% TO STARTPT% + MDLEND% \ PPP&  
  PLTMDL(I) = MDLCRV(C) * 1E+09 * SDIV!  
  C = C + PPP&  
NEXT I  
'PLOT THE ENTIRE MODEL ARRAY  
PY% = YOFFS% - (0 - AMIN%) / (AMAX% - AMIN%) * YMULT%  
PSET (40, PY%)  
FOR J = 0 TO 5999 STEP 10  
  I = J / 10 + 40  
  PY% = YOFFS% - (PLTMDL(J) - AMIN%) / (AMAX% - AMIN%) * YMULT%  
  LINE -(I, PY%)  
NEXT J  
INPUT "ERASE MODEL CURVE(S)"; B$  
IF UCASE$(B$) = "Y" THEN  
  SCREEN 0  
  CALL SCREENINIT  
  FOR I = 40 TO 639  
    PY% = YOFFS% - (PLOTAR(I - 40) - AMIN%) / (AMAX% - AMIN%) *  
    YMULT%  
    PSET (I, PY%)  
  NEXT I
```

```

    FOR J = 0 TO 5999: PLTMDL(J) = 0: NEXT J
END IF
END SUB

SUB PLOTDATA
SCREEN 0
DEV$ = "PLOTTER"
PLO% = ILFIND(DEV$)
    X$ = "TIME / s"
    Y$ = "CURRENT / nA"
    PYMAX! = 8.95
    PYMIN! = -.25
    PXMIN! = 0
    PXMAX! = (HP% - LP%) / 1000
    WRT$ = "IN;SI.18,.27;VS5;RO90;"
    CALL IBWRT(PLO%, WRT$)
    WRT$ = "IP1280,1800,6780,5375;SC0,10000,0,10000;SP1;"
    CALL IBWRT(PLO%, WRT$)
    XTP! = -1100: XLP! = -550: YTP! = -1200: YLP! = -900
AXLABEL:
'This section gets numeric labels for the axes.
'There three labels for the x-axis and four labels
'for the y-axis.
    LX1! = (PXMIN! * 100) / 100
    LX2! = ((PXMAX! - PXMIN!) * 50) / 100 + LX1!
    LX3! = (PXMAX! * 100) / 100
    LY1! = (PYMIN! * 100) / 100
    LY2! = ((PYMAX! - PYMIN!) * 30) / 100 + LY1!
    LY3! = ((PYMAX! - PYMIN!) * 70) / 100 + LY1!
    LY4! = (PYMAX! * 100) / 100
'Draw axes with plotter, using pen 1.

    WRT$ = "PA0,0;TL1,0;PD;XT;": CALL IBWRT(PLO%, WRT$)
    WRT$ = "PR1000,0;XT;"
    FOR I = 1 TO 10
        CALL IBWRT(PLO%, WRT$)
    NEXT I
    WRT$ = "PU;PA0,0;PD;YT;": CALL IBWRT(PLO%, WRT$)
    WRT$ = "PR0,1000;YT;"
    FOR I = 1 TO 10
        CALL IBWRT(PLO%, WRT$)
    NEXT I
'Label x-axis with title and values
    WRT$ = "SP2;PU;PA4200," + VARSTR$(XTP!) + ";LB" + X$ + CHR$(3)
    CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA0," + VARSTR$(XLP!) + ";LB" + VARSTR$(LX1!) + CHR$(3)
    CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA4700," + VARSTR$(XLP!) + ";LB" + VARSTR$(LX2!) +
CHR$(3)
    CALL IBWRT(PLO%, WRT$)
    WRT$ = "PA9700," + VARSTR$(XLP!) + ";LB" + VARSTR$(LX3!) +
CHR$(3)
    CALL IBWRT(PLO%, WRT$)

```

```

'Label y-axis with title and values
  WRT$ = "PA" + VARSTR$(YTP!) + ",3400;DI0,1;LB" + Y$ + CHR$(3)
  CALL IBWRT(PLO%, WRT$)
  WRT$ = "DI;PA" + VARSTR$(YLP!) + ",0;LB" + VARSTR$(LY1!) +
CHR$(3)
  CALL IBWRT(PLO%, WRT$)
  WRT$ = "PA" + VARSTR$(YLP!) + ",3000;LB" + VARSTR$(LY2!) +
CHR$(3)
  CALL IBWRT(PLO%, WRT$)
  WRT$ = "PA" + VARSTR$(YLP!) + ",7000;LB" + VARSTR$(LY3!) +
CHR$(3)
  CALL IBWRT(PLO%, WRT$)
  WRT$ = "PA" + VARSTR$(YLP!) + ",10000;LB" + VARSTR$(LY4!) +
CHR$(3)
  CALL IBWRT(PLO%, WRT$)
  WRT$ = "PA0,0;": CALL IBWRT(PLO%, WRT$)
INPUT "LINE TYPE FOR DATA"; LT$
  IF UCASE$(LT$) = "D" THEN
    WRT$ = "LT0;": CALL IBWRT(PLO%, WRT$)
  END IF
DEF SEG = VARSEG(ADDAT0(0))
OFFS% = VARPTR(ADDAT0(0))
INCR% = 1
IF HP% - LP% - 1 > 15000 THEN INCR% = 2
FOR I = LP% TO HP% - 1
  T% = (I) * 2 * INCR% + OFFS%
  HBYTE% = PEEK(T%)
  LBYTE% = PEEK(T% + 1)
  ADDAT% = (HBYTE% * 256%) + LBYTE%
  IF ADDAT% > 32767 THEN ADDAT% = ADDAT% - 65536
  CUR! = ADDAT% / SDIV!
  YARR!(I - LP%) = CUR!
  XARR!(I - LP%) = I - LP%
NEXT I
CALL XYPLOT(XARR!(), YARR!(), PPP%)
INPUT "INCLUDE MODEL ARRAY"; A$
IF UCASE$(A$) = "Y" THEN
  FOR I = 0 TO 5999
    YARR!(I) = PLTMDL(I) / SDIV!
    IF I = 3000 THEN PRINT YARR!(I)
    XARR!(I) = I
  NEXT I
  WRT$ = "LT;": CALL IBWRT(PLO%, WRT$)
  CALL XYPLOT(XARR!(), YARR!(), 10)
END IF
CALL SCREENINIT
END SUB

SUB SCREENINIT
SCREEN 2
LINE (100, 100)-(120, 100)
LINE (110, 95)-(110, 105)
GET (100, 95)-(120, 105), IMAGE

```



```

PUT (100, 95), IMAGE, XOR
VIEW SCREEN (40, 0)-(639, 167), , 1
VIEW PRINT 23 TO 24
END SUB

```

```

SUB SCREENPLOT

```

```

ARCHOOSE:

```

```

INPUT "PLOT FILE (999) TO EXIT"; F%

```

```

SELE:

```

```

SELECT CASE F%

```

```

    CASE 1

```

```

        DEF SEG = VARSEG(ADDAT0(0))

```

```

        OFFS% = VARPTR(ADDAT0(0))

```

```

    CASE 999

```

```

        GOTO CLOSER1

```

```

    CASE ELSE

```

```

        INPUT "SELECT FILE 1 OR 999 TO EXIT"; F%: GOTO SELE

```

```

    END SELECT

```

```

INPUT "POINTS PER PIXEL"; PPP%

```

```

INPUT "STARTING POINT"; SP%

```

```

LP% = SP% - 1

```

```

HP% = LP% + (PPP% * 600)

```

```

IF HP% > FPTS% - 1 THEN HP% = FPTS% - 1

```

```

CONVERT:

```

```

RP% = 0

```

```

PPP% = (HP% - LP%) / 600

```

```

AMAX% = 1

```

```

AMIN% = 5000

```

```

FOR I = LP% TO (HP% - 1) STEP PPP%

```

```

    T% = 2 * I + OFFS%

```

```

    HBYTE% = PEEK(T%)

```

```

    LBYTE% = PEEK(T% + 1)

```

```

    ADDAT% = (HBYTE% * 256) + LBYTE%

```

```

    IF ADDAT% > 32767 THEN ADDAT% = ADDAT% - 65536

```

```

    ADC% = CINT(ADDAT%)

```

```

    PLOTAR((I - LP%) / PPP%) = ADC%

```

```

    IF ADC% > AMAX% THEN AMAX% = ADC% + 1

```

```

    IF ADC% < AMIN% THEN AMIN% = ADC%

```

```

NEXT I

```

```

CHOICE:

```

```

'PLOT DATA ARRAY ON SCREEN

```

```

CALL SCREENINIT

```

```

IF RP% = 1 THEN GOTO CONVERT

```

```

FOR I = 40 TO 639

```

```

    PY% = YOFFS% - (PLOTAR(I - 40) - AMIN%) / (AMAX% - AMIN%) *

```

```

    YMULT%

```

```

    PSET (I, PY%)

```

```

NEXT I

```

```

INPUT "CONTINUE SERIES, SCAN OR EXIT (A,Y,S,E,P)"; A$

```

```

IF UCASE$(A$) = "Y" THEN

```

```

    LP% = HP%

```

```

    HP% = HP% + (PPP% * 600)

```

```

    IF HP% > 29999 THEN PRINT "OUT OF RANGE": GOTO CHOICE

```

```

        CLS 1: GOTO CONVERT
    ELSEIF UCASE$(A$) = "S" THEN
        CALL SKANSKRN: GOTO CHOICE
    ELSEIF UCASE$(A$) = "P" THEN
        CALL PLOTDATA: GOTO CHOICE
    ELSEIF UCASE$(A$) = "A" THEN
        INPUT "filename for ascii dump"; F$
        OPEN F$ FOR OUTPUT AS #10
        FOR I = 0 TO 599
            WRITE #10, PLOTAR(I), PLTMDL(I * 10)
        NEXT I
        CLOSE #10
    END IF
    CLS 1
    GOTO ARCHOOSE

CLOSER1:
SCREEN 0: CLS
END SUB

SUB SKANSKRN
FOR J = 0 TO 5999: PLTMDL(J) = 0: NEXT J
SELECTX:
PRINT "MIN. FILE POINT "; LP&; " MAX FILE POINT "; HP&
INPUT "STARTING X POINT"; PX&
IF PX& < LP& OR PX& > HP& THEN BEEP: GOTO SELECTX
ON ERROR GOTO 2000
' MOTION LOOP
IMAGPUT:
SPX% = (PX& - LP&) / PPP& + 40
SPY% = YOFFS% - (PLOTAR(SPX% - 40) - AMIN%) / (AMAX% - AMIN%) * YMULT%
PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
DO
    A$ = INKEY$
    SELECT CASE A$
        CASE IS = "P"
            PRINT PX&, (PLOTAR(SPX% - 40)) / SDIV!
            CASE IS = "H"
                IF SPX% > 60 THEN
                    PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
                    SPX% = SPX% - 10
                EXIT DO
            END IF
        CASE IS = "L"
            IF SPX% < 629 THEN
                PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
                SPX% = SPX% + 10
            EXIT DO
            END IF
        CASE IS = "Q"
            GOTO CLOSER2
        CASE IS = "J"
            PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
            PX& = PX& - 1: GOTO IMAGPUT
    
```

```

CASE IS = "K"
    PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
    PX% = PX% + 1: GOTO IMAGPUT
CASE IS = "1"
    LMARK% = PX%: PRINT LMARK%
CASE IS = "2"
    RMARK% = PX%: PRINT RMARK%
CASE IS = "5"
    TMARK% = PX%: PRINT TMARK%
CASE IS = "I"
    IF RMARK% <= LMARK% THEN
        PRINT "ERROR IN MARKING"
    ELSE PRINT USING "###.###"; FILEINT#(LMARK%, RMARK%, 1)
    END IF
CASE IS = "D"
    PRINT LSTEXP!(LMARK%, TMARK%)
CASE IS = "S"
    IF RMARK% <= LMARK% THEN
        PRINT "ERROR IN MARKING"
    END IF
CASE IS = "M"
    CALL LUNSIM(LMARK%, RMARK%, TMARK%, MDLCRV(), MDLEND%)
    CALL MODSPLOT(LMARK%)
    EXIT DO
CASE IS = "R"
    LP% = PX%
    PUT (SPX% - 10, SPY% - 5), IMAGE, XOR
    INPUT "Replot selected, total points"; DELT%
    HP% = LP% + DELT%
    IF HP% > FPT% - 1 THEN HP% = FPT% - 1
    RP% = 1
    GOTO CLOSER2
CASE ELSE
    END SELECT
LOOP
PX% = ((SPX% - 40) * PPP%) + LP%
GOTO IMAGPUT
CLOSER2:
CLS
END SUB

FUNCTION VARSTR$ (IN!)
    D = 1
    XP$ = STR$(IN!)
    VTR$ = LTRIM$(RTRIM$(XP$))
    FOR I = 1 TO LEN(VTR$)
        IF MID$(VTR$, I, 1) = "." THEN VARSTR$ = MID$(VTR$, 1, I + 2): D
        = -1
        IF I = LEN(VTR$) AND D = 1 THEN VARSTR$ = VTR$
    NEXT I
    IF ABS(IN!) < .1 THEN VARSTR$ = "0"
END FUNCTION

```

```

SUB XYPLOT (XARR!(), YARR!(), IFUL&)
  WRT$ = "SP3;VS5;PU;": CALL IBWRT(PLO%, WRT$)
  DIVIDER& = (HP& - LP& - 1) * (IFUL& / PPP&)
  FOR I = 0 TO DIVIDER&
    XP! = (XARR!(I) / DIVIDER&) * 10000
    YP! = (YARR!(I) - PYMIN!) / (PYMAX! - PYMIN!) * 10000
    WRT$ = "PA" + VARSTR$(XP!) + "," + VARSTR$(YP!) + ";PD;"
    CALL IBWRT(PLO%, WRT$)
  NEXT I
  WRT$ = "PA;SP0;PA0,0;": CALL IBWRT(PLO%, WRT$)
END SUB

```

Code for LUNSIM module of LUNFIT.BAS:

```

'MODULE LUNF2
DECLARE FUNCTION INTER! (ARR!())
DECLARE FUNCTION LSTEXP! (L&, M&)
DECLARE FUNCTION FILEINT# (L&, R&, CHK)
DECLARE FUNCTION ASIN! (X!)
DECLARE FUNCTION ACOS! (X!)
DECLARE FUNCTION CHG! (PY1!)
DECLARE FUNCTION CURII! (X1!, Y1!, XP1!, YP1!)
DECLARE FUNCTION CURIII! (X1!, Y1!, XP1!, YP1!)
DECLARE FUNCTION CURIIII! (XP1!, YP1!, XTP1!, YTP1!)
DECLARE FUNCTION GETDI (L&, R&)
DECLARE FUNCTION SQDIST! (X1!, X2!, Y1!, Y2!)
DECLARE FUNCTION XCURVE! (PY1!)
DECLARE SUB LUNSIM (L&, R&, M&, MDLCRV(), MDLEND%)
DECLARE SUB BOTSOL (PY1!, X1!, Y1!, S%)
DECLARE SUB EPS (L!, F$, E!)
DECLARE SUB PARSET (L&, R&, M&)
'DOUBLE LETTERS DENOTE SQUARED SINGLE LETTERS
'VARIABLES ARE AS FOLLOWS: A!, MAJOR AXIS LENGTH; B!, MINOR AXIS LENGTH
'D!, DISTANCE TO LINE EDGE FROM ORIGIN; RA!, RADIUS OF
CRYSTAL(RA2!=RA!^2).
DIM SHARED A!, B!, AA!, BB!, E!, D!, RA!, RA2!, EP!, SPX!, SPY!,
RATECHG!
DIM SHARED MDLCRV(6000) AS SINGLE
DIM F$(10)
CONST PI = 3.1415927#
END

```

```

FUNCTION ACOS! (X!)
  IF X! >= 1! THEN
    ACOS! = 0
  ELSE
    ACOS! = PI / 2 - ATN(X! / (SQ(1 - X! ^ 2)))
  END IF
END FUNCTION

```

```

FUNCTION ASIN (X!)
  IF X! >= 1! THEN
    ASIN! = PI / 2
  ELSE
    ASIN! = ATN(X! / (SQR(1 - X! ^ 2)))
  END IF
END FUNCTION

SUB BOTSOL (PY1!, X1!, Y1!, S%)
  'THIS SUB GETS INTERSECTION POINTS OF THE GROWING MONOLAYER ORIGINATING
  FROM
  'SPX, SPY AND THE ELLIPTICAL BOUNDARY. IT USES A LOGARITHMIC RECURSIVE
  TECH-
  'NIQUE TO OBTAIN A SOLUTION WHICH IS CORRECT WITHIN SOME ERROR, EP!.

  XC! = XCURVE!(PY1!)           'X POINT ON BOUNDARY FOR Y POINT
  DI! = SQDIST!(XC!, SPX!, PY1!, SPY!) 'SQUARED DISTANCE FROM XTAL ORIGIN
  ORSIGN = SGN(DI! - RA2!)      'SIGN OF DIFFERENCE
  IF ABS(DI! - RA2!) < EP! THEN GOTO DONE
  STPSIZ! = 1000 * S%
  REP:                          'BEGIN RECURSION LOOP
  DO
    PY1! = PY1! + STPSIZ!
    XC! = XCURVE!(PY1!)
    DI! = SQDIST!(XC!, SPX!, PY1!, SPY!) 'SQUARED DISTANCE FROM XTAL
    ORIGIN
    NSIGN = SGN(DI! - RA2!)          'CALC NEW SIGN OF DIFFERENCE
    IF ORSIGN <> NSIGN THEN          'COMPARE W/OLD TO SEE IF PAST
    SOLUTION
      IF ABS(DI! - RA2!) < EP! THEN EXIT DO 'WITHIN EPSILON,
    EXIT.
      PY1! = PY1! - STPSIZ!          'BACK UP AND USE SMALLER STEPS
      STPSIZ! = STPSIZ! / 10
    END IF
  LOOP
  'DONE, SET SOLUTION VALUES EQUAL TO X1!, Y1!
  DONE:
  X1! = CSNG(XC!)
  Y1! = CSNG(PY1!)
  END SUB

FUNCTION CURI! (X1!, Y1!, XP1!, YP1!)
  IF RA2! = 0 THEN
    CURI! = 0
  ELSE
    THETA! = 2 * ASIN(SQR(SQDIST!(X1!, XP1!, Y1!, YP1!)) / (2 * RA!))
    CURI! = RATECHG! * RA! * THETA!
  END IF
END FUNCTION

FUNCTION CURII! (X1!, Y1!, XP1!, YP1!)
  THETA! = 2 * ASIN(SQR(SQDIST!(X1!, XP1!, Y1!, YP1!)) / (2 * RA!))

```

```

    CURII! = RATECHG! * RA! * (THETA! - 2 * ACOS((SPX! - D!) / RA!))
END FUNCTION

FUNCTION CURIII! (XP1!, YP1!, XTP1!, YTP1!)
    CURIII! = RATECHG! * RA! * 2 * ASIN(SQR(SQDIST!(XP1!, XTP1!, YP1!,
YTP1!)) / (2 * RA!))
END FUNCTION

SUB EPS (L!, F$, E!)
    'THIS SUBROUTINE DETERMINES MAJOR AND MINOR AXIS LENGTHS OF AN ELLIPSE.
    IF E! = 0! THEN AA! = L! ^ 2: BB! = AA!: GOTO EPSCLOSE    'A CIRCLE.
    IF F$ = "MA" THEN
        'MAJOR AXIS SPECIFIED BY L!.
        C! = E! * L!
        AA! = L! ^ 2
        CC! = C! ^ 2
        BB! = AA! - CC!
    ELSEIF F$ = "MI" THEN
        'MINOR AXIS SPECIFIED BY L!.
        BB! = L! ^ 2
        CC! = BB! / ((1 / (E! ^ 2)) - 1)
        AA! = BB! + CC!
    END IF
    EPSCLOSE:
        A! = SQR(AA!)
        B! = SQR(BB!)
        'MAJOR AXIS LENGTH
        'MINOR AXIS LENGTH.
END SUB

FUNCTION GETD! (L&, R&)
    'THIS FUNCTION DETERMINES D!, FIRST IT TAKES A CIRCLE APPROXIMATION,
    THEN IT
    'DECREASES D! TO GET THE CORRECT AREA FOR THE ELLIPTICAL CASE.
    AREA! = FILEINT#(L&, R&, 1) * 4.50054E+08
    THETA! = (12 * AREA! / AA!) ^ .33333#
    'GET LOWER BOUND FOR THETA
    THETA
    STPSIZ = .1
    THETA! = THETA! - STPSIZ
    DO
        THETA! = THETA! + STPSIZ
        K! = AA! * (THETA! - SIN(THETA!)) / 2
        IF K! > AREA! THEN
            THETA! = THETA! - STPSIZ
            STPSIZ = STPSIZ / 10
            IF STPSIZ < .00001 THEN EXIT DO
        END IF
    LOOP
    D! = A! * COS(THETA! / 2)
    IF E! = 0! THEN
        'RESULT FOR CIRCULAR BOUNDARY.
        GETD! = D!
    ELSEIF E! <> 0 THEN
        'DECREASE D! TO INCREASE AREA.
        STPSIZ = 100
        'THIS SECTION APPROXIMATES THE ELLIPSE SEGMENT AREA BY TAKING HALF THE AREA

```

'AND SUBTRACTING THE AREA OF A TRAPEZOID AND TWO SMALL APPROX. CIRCULAR
'SEGMENTS. THE TRAPEZOID AREA CHANGES WITH D1, BUT CIRC. SEGS ARE
ASSUMED NOT
'TO CHANGE DRAMATICALLY WITH A SMALL D1 CHANGE. THIS WILL PRODUCE
SIGNIFICANT
'ERROR FOR LARGE E1.

DO

D1 = D1 - STPSIZ
SECTH1 = PI / 2 - ACOS(D1 / A1)
SECAR1 = AA1 * (SECTH1 - SIN(SECTH1))
K1 = PI / 2 * A1 * B1 - (1 + SQR(1 - (D1 ^ 2) / AA1)) * B1 * D1 -

SECAR1

IF K1 > AREA1 THEN
D1 = D1 + STPSIZ
STPSIZ = STPSIZ / 10
IF STPSIZ < .01 THEN EXIT DO

END IF

LOOP

GETD1 = D1

'APPROX. RESULT FOR

ELLIP. BND.

END IF

END FUNCTION

FUNCTION INTER1 (ARR1())

SUM1 = 0

FOR I = 0 TO 600

SUM1 = SUM1 + ARR1(I) * .001

NEXT I

INTER1 = SUM1

END FUNCTION

SUB LUNSIM (L&, R&, M&, MDLCRV(), MDLEND%)

FLAG% = 0

START:

CALL PARSET(L&, R&, M&)

INPUT "OFFSET FROM MAX IN UNITS OF nm "; OPX1: SPX1 = A1 - OPX1

SPY1 = SQR(BB1 * (1 - SPX1 ^ 2 / AA1))

PY11 = SPY1: PYP11 = SPY1: EP1 = 1000

MDLCRV(0) = 01

X11 = 0: Y11 = 0: XP11 = 0: YP11 = 0

H1 = A1 - D1

'COMPUTE SPACING IN nm PER 0.1 ms POINT USING INPUT EXPANSION RATE

SCALE1 = LSTEXP1(L&, M&) * 10001

INPUT "NUMBER OF SIMULATION POINTS IS SELECTED HERE"; FUL%

FOR I = 0 TO 5999 STEP FUL%

RA1 = I * SCALE1

RA21 = RA1 ^ 2

IF RA1 <= H1 - OPX1 THEN

'CURRENT REGIEME 1

CALL BOTSOL(PY11, X11, Y11, 1)'GET INC Y SOLUTION

CALL BOTSOL(PYP11, XP11, YP11, -1)'GET DEC Y SOLUTION

MDLCRV(I) = CUR11(X11, Y11, XP11, YP11)

PY11 = Y11: PYP11 = YP11

ELSEIF RA1 > H1 - OPX1 THEN

'INTERACTING WITH LINE ALSO

```

      CALL BOTSOL(PYP11, XP11, YP11, -1)
      IF XP11 < D1 THEN GOTO ARFILL 'DONE GROWING FILL ARRAY
      IF X11 >= D1 THEN                'STILL IN REGIEME 2
        CALL BOTSOL(PY11, X11, Y11, 1)
        MDLCRV(I) = CURIII(X11, Y11, XP11, YP11)
        PY11 = Y11: PYP11 = YP11
      ELSEIF X11 < D1 THEN                'ONLY ONE SIDE LEFT, REGIEME 3
        EP1 = 1000
        XTP11 = D1
        YTP11 = SPY1 - SQR(RA21 - (D1 - SPX1) ^ 2)
        MDLCRV(I) = CURIIII(XP11, YP11, XTP11, YTP11)
        PYP11 = YP11
      END IF
    END IF
  NEXT I
ARFILL:
FOR F = I TO 599
  MDLCRV(F) = 01
NEXT F
MDLEND% = I + 1
END SUB

SUB PARSET (L&, R&, M&)
INPUT "ECCENTRICITY "; E1
L1 = 381001: F$ = "MI"
CALL EPS(L1, F$, E1)
H1 = A1 - GETD1(L&, R&)
RATECHG1 = LSTEXP1(L&, M&) * 1E+07 * 2.216E-18
END SUB

FUNCTION SQDIST1 (X11, X21, Y11, Y21)
  SQDIST1 = ((X11 - X21) ^ 2) + ((Y11 - Y21) ^ 2)
END FUNCTION

FUNCTION XCURVE1 (PY11)
  XCURVE1 = SQR(AA1 * (1 - (PY11 ^ 2) / BB1))
END FUNCTION

```


APPENDIX B

Derivation of equation 2 chapter 1:

□ Consider growth of a new phase 3 from a supersaturated phase 2 onto a substrate phase 1;

relevant surface tensions σ_{12} , σ_{23} , σ_{13} and σ_e are as labeled.

The new phase consists of m particles with "atomic" volume v . The formation of the new phase is an activated process which goes through a critical cluster containing m^* particles. A balance of free energies determines m^* .

□ The total free energy for overpotentials, η , with respect to the equilibrium potential to form a cluster of m particles of like upon like is a sum of volume, surface, edge, and entropy terms;

$$\Delta G(m) = (mv) \left[\frac{-ze\eta}{v} \right] + \left(\frac{mv}{h} \right) \sigma_{13} + 2(m\pi v h)^{1/2} \sigma_e + G_c$$

(B1),

G_c is the surface precursor entropy term. For like upon like, σ_{12} and σ_{23} terms do not appear, σ_{13} is kept to account for stabilization of the

new phase by a defect at the nucleation site. The use of the overpotential to describe the free energy for volume formation reduces the need for inclusion of ionic solvation loss and other issues which control the equilibrium potential. The entropy term has been derived by Lothe and Pound to be $G_c = kT \ln(\Gamma_{Ag^0})$, however, this term is a source of controversy. For this derivation, the functional details of G_c are less important, as long as it is independent of m .

□ Differentiating $\Delta G(m)$ by m and solving for the critical cluster size by setting

$$\left[\frac{\delta \Delta G(m)}{\delta m} \right] = 0, \quad (B2)$$

gives:

$$m^* = \frac{(\pi v h) \sigma_e^2}{[z e \eta - \frac{v}{h} \sigma_{13}]^2} \quad (B3).$$

□ substituting $\Delta G(m^*) = \Delta G^\ddagger$;

$$\Delta G^\ddagger = \frac{(\pi v h) \sigma_e^2}{[z e \eta - \frac{v}{h} \sigma_{13}]} + G_c \quad (B4).$$

□ rate of nucleation A , assuming $\Delta G^\ddagger$ is the activation energy;

$$A = A' \exp \left[- \frac{\Delta G^\ddagger}{kT} \right] = A_0 \exp \frac{\frac{v}{h} e^2}{[\frac{v}{h} \sigma_{13} - z e \eta] kT} \quad (B5).$$

to get the final result, we have substituted a one dimensional edge energy $\varepsilon = \sigma_e h$, for the "edge" tension .

APPENDIX C

ASYST code to generate model curves in sets of 100. For ASYST users, the loading order is first RSIM4.TXT, then CRNS.TXT.

CRNS.TXT (short for "create-n-save"):

```
\ THIS TEXT, WHEN LOADED AFTER RSIM4.TXT OR EQUIVALENT ALLOWS FOR THE
\ GENERATION OF MULTIPLE CURRENT TIME TRANSIENTS FROM RANDOM POINTS
\ WITHIN AN ELLIPTICAL ELECTRODE. RUNNING PROCEDURE IS AS FOLLOWS:
\ 1) LOAD RSIM4.TXT (OR EQUIVALENT)
\ 2) LOAD THIS FILE
\ 3) RUN THIS FILE BY EXECUTING CREATE.N.SAVE
\ THIS PROGRAM NOMINALLY GENERATES AND STORES 100 TRANSIENTS AND THEIR
\ LOCATIONS IN A USER SPECIFIED FILE
```

```
10 STRING FILNAM
REAL SCALAR MLOCK
REAL SCALAR MLOCY
REAL SCALAR LOC
REAL SCALAR B
REAL DIM[ 500 , 25 ] ARRAY ARDATAG
REAL DIM[ 100 , 2 ] ARRAY XYDATA
```

```
: CREATE.N.SAVE
CR ." SPECIFY NAME FOR TRANSIENT FILE: "
"INPUT FILNAM " :=
FILE.TEMPLATE
2 COMMENTS
REAL DIM[ 500 , 25 ] SUBFILE
4 TIMES
REAL DIM[ 100 , 2 ] SUBFILE
2 TIMES
END
FILNAM DEFER> FILE.CREATE
FILNAM DEFER> FILE.OPEN
CR ." ANY COMMENTS ? "
"INPUT 1 >COMMENT
CR ." SEED VALUE ( ANY LEGAL INTEGER )? "
#INPUT SEED :=
ECCEN.PS
CR
5 1 DO
26 1 DO
```

```

      J 25 * 25 - I + LOC := LOC .
      BEGIN
        RAND.UNIF 250 * SPX :=
        SPX DUP * AA / MLOCK :=
        BB SQRT B :=
        RAND.UNIF B * SPY :=
        SPY DUP * BB / MLOCY :=
        MLOCK MLOCY + 1. <=
      UNTIL
      RSIM.MB
      DATAG ARDATAG XSECT[ 1 , I ] :=
      SPX XYDATA [ LOC , 1 ] :=
      SPY XYDATA [ LOC , 2 ] :=
    LOOP
      I SUBFILE
      ARDATAG ARRAY>FILE
    LOOP
      5 SUBFILE
      XYDATA ARRAY>FILE
      FILNAM DEFER> FILE.CLOSE
;

```

RSIM4.TXT:

```

REAL SCALAR R
REAL SCALAR RR
REAL SCALAR II
REAL SCALAR AREA
REAL SCALAR SPX
REAL SCALAR SPY
REAL SCALAR E
REAL SCALAR AA
REAL SCALAR BB
REAL SCALAR CC
REAL DIM[ 500 ] ARRAY DATAG
REAL DIM[ 360 ] ARRAY PTS
REAL DIM[ 360 ] ARRAY CTHETA
REAL DIM[ 360 ] ARRAY STHETA
REAL DIM[ 360 ] ARRAY TPX
REAL DIM[ 360 ] ARRAY TPY
\THIS IS A SIMULATION PROGRAM WHICH MODELS THE GROWTH OF A CIRCLE WITHIN
\AN ELLIPSE. THE ALGORITHM EMPLOYED TAKES A NUMBER OF SPACED POINTS
\WITHIN A SHELL OF UNIT RADIUS AND COMPARES THESE POINTS WITH THE
\ELECTRODE BOUNDARY. THE NUMBER OF POINTS WITHIN THE BOUNDARY IS
\MULTIPLIED BY THE AREA OF THE SHELL TO GET A CHARGE FOR THE DISCRETE
\TIME UNIT. WHEN STORED IN THE ARRAY DATAG, THE RESULTING ARRAY RECORDS
\CURRENT VS. TIME (ARBITRARY UNITS). ECCEN.PS SETS THE PARAMETERS FOR
\THE BOUNDARY GIVEN AN ECCENTRICITY ( E ). INPUT OUTSIDE THE PROGRAM.
\RSIM.MB CARRIES OUT THE GROWTH PROCEDURE AND LEAVES THE i vs. t DATA
\IN SEQUENTIAL ORDER IN DATAG
\CREATE.N.SAVE GENERATES A SET OF 100 TRANSIENTS AND STORES THEN IN A
\DATA FILE WITH PROPER SUBFILE CLASSIFICATION FOR ANALYSIS PROGRAMS.
\THIS FILE CAN BE LOADED BY LOADING CRNS.TXT

```

```

: ECCEN.PS
  CR ." ECCENTRICITY? " #INPUT E :=
  E 250. * DUP * CC :=
  250. DUP * AA :=
  AA CC - BB :=
  0. RR :=
;

: RSIM.MB
  DEG
  360 RAMP COS CTHETA :=
  360 RAMP SIN STHETA :=
  0 PTS := 0. RR := 0 DATAG :=
  501. 1. DO
    I R :=
    R R * II :=
    II RR - AREA :=
    CTHETA R * TPX :=
    STHETA R * TPY :=
    TPX SPX + DUP * TPX := \ SPX & SPY ARE USER INPUT COORDINATES
    TPY SPY + DUP * TPY := \ TO LOCATE THE ORIGINAL NUCLEUS.
    TPX AA / TPX :=
    TPY BB / TPY :=
    TPX TPY + 1. [<=] ^SUM PTS :=
    PTS [ 360 ] AREA * 360 / AREA :=
    AREA DATAG [ I ] :=
    PTS [ 360 ] 0 = IF LEAVE THEN
    0 PTS :=
    II RR :=
  LOOP
;

REAL SCALAR VRMS
: GAUSS.NOISE \ GENERATE NOISE ARRAY WITH STD DEV VRMS
  DIM[ 500 ] REAL UNNAMED.ARRAY
  501 1 DO RAND.NRML OVER [ I ] := LOOP
  VRMS *
;

```

Code which demonstrates a way of extracting critical points from simulated data, PROTM.TXT:

```

\ THIS FILE WILL PROCESS SIMULATED TRANSIENTS GENERATED BY CRNS.TXT OR
\ EQUIVALENT. ALL VARIABLES NEEDED ARE DECLARED WITHIN THIS TEXT.
\ T1 AND T2 ARE STORED IN ORDER IN SUBFILE 5 OF DATA FILE.
\ T1 IS DERIVED FROM THE FIRST DEVIATION FROM LINEAR BEHAVIOR.
\ T2 IS DERIVED BY A FIT THROUGH THE END OF THE CURVE.

```

```

REAL SCALAR R
10 STRING FILNAM
REAL SCALAR LOC
REAL SCALAR II
REAL SCALAR T1
REAL SCALAR T2
REAL SCALAR CON
REAL SCALAR COMPR
REAL SCALAR CONR
REAL SCALAR CONA
REAL SCALAR CONI
REAL SCALAR CONT
REAL DIM[ 2 ] ARRAY LREG
REAL DIM[ 3 ] ARRAY TFIT
REAL DIM[ 3 ] ARRAY IFIT
REAL DIM[ 500 , 25 ] ARRAY ARDATAG
REAL DIM[ 100 , 2 ] ARRAY TIME

: PROCESS
  CR ." WHAT IS THE TRANSIENT FILE NAME? "
  "INPUT FILNAM " :=
  CR ." INITIAL RADIUS? "
  #INPUT CON :=
  CR ." INCREMENT? "
  #INPUT CONI :=
  CR ." AREA FACTOR? "
  #INPUT CONA :=
  CR ." SCALING FACTOR? "
  #INPUT CONT :=
  FILNAM DEFER> FILE.OPEN
5 1 DO
  I SUBFILE
  ARDATAG FILE>ARRAY
26 1 DO
  J 25 * 25 - I + LOC :=
  0 R :=
  CON CONR :=
251 1 DO
  ARDATAG [ I , J ] COMPR :=
  CONR COMPR - .200 > IF LEAVE THEN
  I 1 - T1 :=
  CONR CONI + CONR :=
  LOOP
501 250 DO
  I 3 - II :=
  10. ARDATAG [ I , J ] >= IF
  3 RAMP II + TFIT :=
  4 1 DO
    1 II + II :=
    ARDATAG [ II , K ] IFIT [ I ] :=
  LOOP
  TFIT
  IFIT

```

```

1 LEASTSQ.POLY.FIT LREG :=
0. LREG [ 2 ] - LREG [ 1 ] / R - T2 :=
T2 I > IF I T2 := ." * " THEN
LEAVE THEN
LOOP
T1 CONT / TIME [ LOC , 1 ] :=
T2 CONT / TIME [ LOC , 2 ] :=
LOOP
LOOP
6 SUBFILE
TIME ARRAY>FILE
FILNAM DEFER> FILE.CLOSE
;

```

Code to convert an array of critical times into an array of x and y coordinates of the initial critical cluster, TREVAL.TXT:

```

\THIS PROGRAM CONVERTS SETS OF TIMES STORED IN SUBFILE 6 OF LENGTH
\100 INTO X AND Y COORDINATES, ARRAYS PX AND PY. OPERATION GOES AS
\FOLLOWS:
\      1) CALL ECCEN.PS AND SET ECCENTRICITY AND MINOR AXIS.
\      2) CALL LOADTIMES TO SET FILE AND STORE TIMES IN RR1 AND RR2
\          ARRAYS.
\      3) CALL XYCONV2 WHICH WILL CONVERT THE TIMES INTO COORDINATES
\THE ALGORITHM USED DEFINES AN ELLIPSE UPON WHICH THE NUCLEUS LIES BY
\SUBTRACTING THE FIRST TIME( IN RADIAL UNITS ) FROM THE MAJOR AND MINOR
\AXES. THEN, THE NORMAL TO THE ORIGINAL ELLIPSE OF LENGTH T2 WHICH LIES
\ON THE CALCULATED ELLIPSE IS DETERMINED. THIS POINT OF INTERSECTION IS
\THE LOCATION OF THE INITIAL NUCLEUS.
REAL SCALAR R
REAL SCALAR E
REAL SCALAR AA
REAL SCALAR BB
REAL SCALAR CC
REAL SCALAR A
REAL SCALAR B
REAL SCALAR C
REAL SCALAR PX
REAL SCALAR PY
REAL SCALAR R1
REAL SCALAR T2
REAL SCALAR XPARA
REAL SCALAR YPARA
REAL SCALAR AAP
REAL SCALAR BBP
REAL SCALAR P
REAL SCALAR THETA
REAL DIM[ 100 ] ARRAY APX
REAL DIM[ 100 ] ARRAY APY
REAL DIM[ 100 ] ARRAY RR1
REAL DIM[ 100 ] ARRAY RR2

```



```

REAL DIM[ 100 ] ARRAY RPX
REAL DIM[ 100 ] ARRAY RPY
REAL DIM[ 189 ] ARRAY EPX
REAL DIM[ 189 ] ARRAY EPY
REAL DIM[ 189 ] ARRAY TEMP
REAL DIM[ 100 , 2 ] ARRAY TIME
10 STRING FILNAM

: ECCEN.PS
CR ." ECCENTRICITY? " #INPUT E :=
CR ." MINOR AXIS? " #INPUT DUP * BB :=
E E * NEG 1 + BB SWAP / AA :=
AA BB - CC :=
AA SQRT A :=
BB SQRT B :=
CC SQRT C :=
;

: LOADTIMES
RAD
CR ." NAME OF FILE WITH T1,T2 ? "
"INPUT FILNAM " :=
FILNAM DEFER> FILE.OPEN
6 SUBFILE
TIME FILE>ARRAY
FILNAM DEFER> FILE.CLOSE
TIME XSECT[ 1 , 1 ] RR1 :=
TIME XSECT[ 1 , 2 ] RR2 :=
;

: GETREALDATA
FILNAM DEFER> FILE.OPEN
5 SUBFILE
TIME FILE>ARRAY
FILNAM DEFER> FILE.CLOSE
TIME XSECT[ 1 , 1 ] RPX :=
TIME XSECT[ 1 , 2 ] RPY :=
;

: PUTITTOGETHER
189 RAMP 0.98 + EPY :=
AA BB / EPY * EPY * TEMP :=
AA TEMP - SQRT EPX :=
EPX EPY XY.AUTO.PLOT
;

: DECIDE
RAD
75 T2 :=
T2 NEG XPARA :=
T2 DUP * AA / NEG 1. + SQRT B * NEG YPARA :=
YPARA AA * BB / XPARA / ATAN THETA :=
THETA COS RR2 [ R1 ] * XPARA + PX :=

```

```

    THETA SIN RR2 [ R1 ] * YPARA + PY :=
    PX DUP * AAP / PX :=
    PY DUP * BBP / PY :=
    PX PY + 1. > IF 2 P := THEN
    PX PY + 1. < IF 1 P := THEN
    PX PY + 1. = IF
        THETA COS RR2 [ R1 ] * XPARA + APX [ R1 ] :=
        THETA SIN RR2 [ R1 ] * YPARA + APY [ R1 ] :=
        3 P := THEN
;

: XFIT
    150 0 DO
        I .001 + T2 :=
        T2 NEG XPARA :=
        T2 DUP * AA / NEG 1. + SQRT B * NEG YPARA :=
        YPARA AA * BB / XPARA / ATAN THETA :=
        THETA COS RR2 [ R1 ] * XPARA + PX :=
        THETA SIN RR2 [ R1 ] * YPARA + PY :=
        PX DUP * AAP / XPARA :=
        PY DUP * BBP / YPARA :=
        XPARA YPARA + 1. <= IF 3 P := LEAVE THEN
    LOOP
    PX APX [ R1 ] :=
    PY APY [ R1 ] :=
;

: YFIT
    YPARA 1. + NEG R :=
    R 0 DO
        I .001 + T2 :=
        T2 NEG YPARA :=
        T2 DUP * BB / NEG 1. + SQRT A * NEG XPARA :=
        YPARA AA * BB / XPARA / ATAN THETA :=
        THETA COS RR2 [ R1 ] * XPARA + PX :=
        THETA SIN RR2 [ R1 ] * YPARA + PY :=
        PX DUP * AAP / XPARA :=
        PY DUP * BBP / YPARA :=
        XPARA YPARA + 1. >= IF 3 P := LEAVE THEN
    LOOP
    PX APX [ R1 ] :=
    PY APY [ R1 ] :=
;

: XYCONV2
    101 1 DO
        I R1 :=
        A RR1 [ I ] - DUP * AAP :=
        B RR1 [ I ] - DUP * BBP :=
        DECIDE
        1 P = IF XFIT THEN
        2 P = IF YFIT THEN
    LOOP

```

CR ." DONE. "

;

APPENDIX D

Scanning tunneling microscope electronics schematics. There are a total of 4 circuit cards depicted here. The content of the third card is split into two figures here for clarity. This division is also a logical one because the functionality of board 3 part B will be incorporated into a fifth card which will allow plug-in changes to the feedback mechanism. Captions for the figures will precede the pages which contain the figures themselves.

Figure D1: This circuit amplifies and buffers digital signals from the computer for use in the experiment. The majority of the output lines are used for switching relays elsewhere within the electronics; however, the control signal for the sample-and-hold circuitry is generated here as well. The outputs from the computer interface card, the Metrabyte DDA-06, are not strong enough to drive typical reed relays. High-gain Darlington transistors 2N6039 amplify the current signal from the DDA-06 digital signals to suitable levels. At this revision, there is an excess of drive lines with respect to the total number used, this allows painless expansion to include additional digital controls at a later date.

Figure D1

Figure D2: These three circuit modules all reside on the same card. One purpose of the card is to provide analog control signals to the experiment in the form of coarse PZT control and sample bias. Coarse PZT control signals are generated by an active 2-pole Bessel filter with a 10 second rise-time. The sample bias is generated by adding the control signal from the computer and the signal from the lock-in amplifier. This circuit is designed to begin rolling off signals at 12 kHz. The narrow bandwidth here reduces total noise throughput to the experiment, but also limits the available window for spectroscopic measurements. The other function of this card is to provide a module for subtracting off a constant portion of the vertical control signal. The difference between the control signal and the input analog signal from the computer is multiplied by ten, allowing sensitivity of 1 nm/V. This quantity translates into 5 pm per bit after the analog-to-digital conversion.

CIRCUIT 2

The diagram shows a 74181 ALU chip with its pins connected to a 741 op-amp and various passive components. The ALU pins are: 18 (V_{CC}) to +5V, 16 (V_{EE}) to ground, 15 (A₁) to 0V, 14 (A₂) to 0V, 13 (A₃) to 0V, 12 (A₄) to 0V, 11 (A₅) to 0V, 10 (A₆) to 0V, 9 (A₇) to 0V, 8 (A₈) to 0V, 7 (A₉) to 0V, 6 (A₁₀) to 0V, 5 (A₁₁) to 0V, 4 (A₁₂) to 0V, 3 (A₁₃) to 0V, 2 (A₁₄) to 0V, 1 (A₁₅) to 0V, 0 (A₁₆) to 0V, 17 (A₁₇) to 0V, 19 (A₁₈) to 0V, 20 (A₁₉) to 0V, 21 (A₂₀) to 0V, 22 (A₂₁) to 0V, 23 (A₂₂) to 0V, 24 (A₂₃) to 0V, 25 (A₂₄) to 0V, 26 (A₂₅) to 0V, 27 (A₂₆) to 0V, 28 (A₂₇) to 0V, 29 (A₂₈) to 0V, 30 (A₂₉) to 0V, 31 (A₃₀) to 0V, 32 (A₃₁) to 0V, 33 (A₃₂) to 0V, 34 (A₃₃) to 0V, 35 (A₃₄) to 0V, 36 (A₃₅) to 0V, 37 (A₃₆) to 0V, 38 (A₃₇) to 0V, 39 (A₃₈) to 0V, 40 (A₃₉) to 0V, 41 (A₄₀) to 0V, 42 (A₄₁) to 0V, 43 (A₄₂) to 0V, 44 (A₄₃) to 0V, 45 (A₄₄) to 0V, 46 (A₄₅) to 0V, 47 (A₄₆) to 0V, 48 (A₄₇) to 0V, 49 (A₄₈) to 0V, 50 (A₄₉) to 0V, 51 (A₅₀) to 0V, 52 (A₅₁) to 0V, 53 (A₅₂) to 0V, 54 (A₅₃) to 0V, 55 (A₅₄) to 0V, 56 (A₅₅) to 0V, 57 (A₅₆) to 0V, 58 (A₅₇) to 0V, 59 (A₅₈) to 0V, 60 (A₅₉) to 0V, 61 (A₆₀) to 0V, 62 (A₆₁) to 0V, 63 (A₆₂) to 0V, 64 (A₆₃) to 0V, 65 (A₆₄) to 0V, 66 (A₆₅) to 0V, 67 (A₆₆) to 0V, 68 (A₆₇) to 0V, 69 (A₆₈) to 0V, 70 (A₆₉) to 0V, 71 (A₇₀) to 0V, 72 (A₇₁) to 0V, 73 (A₇₂) to 0V, 74 (A₇₃) to 0V, 75 (A₇₄) to 0V, 76 (A₇₅) to 0V, 77 (A₇₆) to 0V, 78 (A₇₇) to 0V, 79 (A₇₈) to 0V, 80 (A₇₉) to 0V, 81 (A₈₀) to 0V, 82 (A₈₁) to 0V, 83 (A₈₂) to 0V, 84 (A₈₃) to 0V, 85 (A₈₄) to 0V, 86 (A₈₅) to 0V, 87 (A₈₆) to 0V, 88 (A₈₇) to 0V, 89 (A₈₈) to 0V, 90 (A₈₉) to 0V, 91 (A₉₀) to 0V, 92 (A₉₁) to 0V, 93 (A₉₂) to 0V, 94 (A₉₃) to 0V, 95 (A₉₄) to 0V, 96 (A₉₅) to 0V, 97 (A₉₆) to 0V, 98 (A₉₇) to 0V, 99 (A₉₈) to 0V, 100 (A₉₉) to 0V, 101 (A₁₀₀) to 0V, 102 (A₁₀₁) to 0V, 103 (A₁₀₂) to 0V, 104 (A₁₀₃) to 0V, 105 (A₁₀₄) to 0V, 106 (A₁₀₅) to 0V, 107 (A₁₀₆) to 0V, 108 (A₁₀₇) to 0V, 109 (A₁₀₈) to 0V, 110 (A₁₀₉) to 0V, 111 (A₁₁₀) to 0V, 112 (A₁₁₁) to 0V, 113 (A₁₁₂) to 0V, 114 (A₁₁₃) to 0V, 115 (A₁₁₄) to 0V, 116 (A₁₁₅) to 0V, 117 (A₁₁₆) to 0V, 118 (A₁₁₇) to 0V, 119 (A₁₁₈) to 0V, 120 (A₁₁₉) to 0V, 121 (A₁₂₀) to 0V, 122 (A₁₂₁) to 0V, 123 (A₁₂₂) to 0V, 124 (A₁₂₃) to 0V, 125 (A₁₂₄) to 0V, 126 (A₁₂₅) to 0V, 127 (A₁₂₆) to 0V, 128 (A₁₂₇) to 0V, 129 (A₁₂₈) to 0V, 130 (A₁₂₉) to 0V, 131 (A₁₃₀) to 0V, 132 (A₁₃₁) to 0V, 133 (A₁₃₂) to 0V, 134 (A₁₃₃) to 0V, 135 (A₁₃₄) to 0V, 136 (A₁₃₅) to 0V, 137 (A₁₃₆) to 0V, 138 (A₁₃₇) to 0V, 139 (A₁₃₈) to 0V, 140 (A₁₃₉) to 0V, 141 (A₁₄₀) to 0V, 142 (A₁₄₁) to 0V, 143 (A₁₄₂) to 0V, 144 (A₁₄₃) to 0V, 145 (A₁₄₄) to 0V, 146 (A₁₄₅) to 0V, 147 (A₁₄₆) to 0V, 148 (A₁₄₇) to 0V, 149 (A₁₄₈) to 0V, 150 (A₁₄₉) to 0V, 151 (A₁₅₀) to 0V, 152 (A₁₅₁) to 0V, 153 (A₁₅₂) to 0V, 154 (A₁₅₃) to 0V, 155 (A₁₅₄) to 0V, 156 (A₁₅₅) to 0V, 157 (A₁₅₆) to 0V, 158 (A₁₅₇) to 0V, 159 (A₁₅₈) to 0V, 160 (A₁₅₉) to 0V, 161 (A₁₆₀) to 0V, 162 (A₁₆₁) to 0V, 163 (A₁₆₂) to 0V, 164 (A₁₆₃) to 0V, 165 (A₁₆₄) to 0V, 166 (A₁₆₅) to 0V, 167 (A₁₆₆) to 0V, 168 (A₁₆₇) to 0V, 169 (A₁₆₈) to 0V, 170 (A₁₆₉) to 0V, 171 (A₁₇₀) to 0V, 172 (A₁₇₁) to 0V, 173 (A₁₇₂) to 0V, 174 (A₁₇₃) to 0V, 175 (A₁₇₄) to 0V, 176 (A₁₇₅) to 0V, 177 (A₁₇₆) to 0V, 178 (A₁₇₇) to 0V, 179 (A₁₇₈) to 0V, 180 (A₁₇₉) to 0V, 181 (A₁₈₀) to 0V, 182 (A₁₈₁) to 0V, 183 (A₁₈₂) to 0V, 184 (A₁₈₃) to 0V, 185 (A₁₈₄) to 0V, 186 (A₁₈₅) to 0V, 187 (A₁₈₆) to 0V, 188 (A₁₈₇) to 0V, 189 (A₁₈₈) to 0V, 190 (A₁₈₉) to 0V, 191 (A₁₉₀) to 0V, 192 (A₁₉₁) to 0V, 193 (A₁₉₂) to 0V, 194 (A₁₉₃) to 0V, 195 (A₁₉₄) to 0V, 196 (A₁₉₅) to 0V, 197 (A₁₉₆) to 0V, 198 (A₁₉₇) to 0V, 199 (A₁₉₈) to 0V, 200 (A₁₉₉) to 0V, 201 (A₂₀₀) to 0V, 202 (A₂₀₁) to 0V, 203 (A₂₀₂) to 0V, 204 (A₂₀₃) to 0V, 205 (A₂₀₄) to 0V, 206 (A₂₀₅) to 0V, 207 (A₂₀₆) to 0V, 208 (A₂₀₇) to 0V, 209 (A₂₀₈) to 0V, 210 (A₂₀

CIRCUIT b

5 μ F

100 Ω

OP-27

37k Ω

100k Ω

100k Ω

1.8k Ω

5 μ F

ΔZ MON $\times 10$

ΔZ MON $\times 10$

Z MONITOR

DAC4 SIC

CIRCUIT C

DAC02 CH1

1.8kΩ

5μF

20kΩ

13.3kΩ

49.9kΩ

OP-07

13.3kΩ

29kΩ

49.9kΩ

5μF

TO BERTAN
0-5V I/P

CORRESPONDING APPROACH CONTROL
64C INPUT TO 2-POLE BESSSEL FILTER (1Hz CUT-OFF)

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Figure D3: This circuit is the first part of the total circuit on board 3. This part takes analog inputs from the computer via the DDA-06 interface card and converts them into the drive signals for the scanning piezoelectric elements. Scan signals in x and y directions are scaled and multiplied by -1 in the first stage of the analog computer, on the upper left of the figure. The scaled signals and their complements are combined with the vertical control signal in the three summing amplifiers (OP-27 operational amplifiers). Each summing amplifier sends output to its own high-voltage amplifier which scales the signal 25 times. Since piezoelectric elements contract with increasing voltage, the most positive signal to the elements comes from the power supply, and the "return" comes from the output of the high-voltage amplifier. With this configuration, the maximum signal corresponds to almost zero voltage applied across the element, resulting in maximum extension. The dual-amplifier circuit at the bottom of this figure is an active 4-pole Bessel filter with a rise-time of 1 second. This filter is to block computer noise on the signal which determines the tunneling current feedback level. The 4-pole Bessel filter provides very steep roll-off compared to RC filters and is very effective.

BOARD 3 ANALOG COMPUTER/SCAN SYSTEM AND Z CONTROL

PART A:

Figure D3

Figure D4: Part B of the circuit on board 3. This is the circuitry that is responsible for vertical control via feedback. The tunneling current and control signals are compared with a high-speed comparator. The comparator is powered by voltage regulators to prevent high-speed oscillations in the supply rails. An integrator follows the comparator, this component is the slow link in the feedback loop to ensure stability. Output from the integrator produces vertical deflections of 10 nm per volt. A twin-T notch filter centered at 5.8 kHz (-60 dB) after the integrator counteracts a resonance in the scanning PZT. The comparator/integrator feedback system allows for better loop response speed control while keeping good small signal compensation. Simple integrator circuits tend to lose the small signal response required to maintain junction stability when long rise-times are used. The sample/hold amplifier is usually kept in follower mode, allowing transmission of the integrator signal. The amplifier is set in hold mode for operation in fixed height mode. The last amplifier adds the output from the integrator to a constant offset, which places the scanning elements at nominally half-extension, allowing for travel to produce scan deflections.

BOARD 3 ANALOG COMPUTER/SCAN SYSTEM AND Z CONTROL PART B:

Figure D4

Figure D5: This board houses the current-to-voltage conversion and tunneling current signal processing circuitry. A dual operational amplifier is used for current-to-voltage conversion and buffering the guard line in the current lead. The output from the current-to-voltage converter is passed through an a.c. bandpass filter which allows detection of rapidly changing components of the tunneling current. This can be used for detection of small signal conductance or current corrugations from fixed height scans. The current-to-voltage converter also sends a signal to an optional inverter. The optional inverter is used to keep the proper sign of the tunneling current signal going to the feedback circuitry. The output of the optional inverter goes both to the feedback circuitry and external monitors of the d.c. current.

[illegible]

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END

**DATE
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