

Investigating surface interactions of Pb on Ge(111) using STM

Piper Aislinn

NSF Physics REU, UC Davis

ABSTRACT: Using scanning tunneling microscopy to investigate the nucleation and growth of islands of Pb on Ge(111) surfaces will provide further insight into quantum size effects observed in previous experiments involving Pb on Si(111) surfaces that lead to favored island heights. My work this summer served to identify and begin solving a variety of mechanical issues that were preventing the capture of atomic resolution images.

1. INTRODUCTION

Surface science is critical to the development of cutting edge technology, including electronics and nanotechnology. Surface behavior and interactions are far more complex than bulk characteristics due to the discontinuity in the periodic crystal structure at the vacuum interface, as well as the domination of the quantum regime in one- and two-dimensional materials. By understanding the surface interactions between semiconductors and metals, we can control the growth and properties of nanostructures more effectively. In addition, linking meso- and nanoscale behaviors allows us to bridge the gaps between classical and quantum regimes.

Scanning tunneling microscopy (STM) was invented in 1981 by Gerd Binnig and Heinrich Rohrer at the IBM Zurich Research Laboratory [1]. It was the first technology that allowed us to view flat materials on the atomic scale. Since its invention, it has been used to study surfaces surrounded by vacuum, gases, or solutions. It is a powerful tool for condensed matter and materials physics and has allowed us to visualize and make more tangible the strange world of the atomic regime.

2. BACKGROUND

Professor Chiang's group is investigating the behavior of metals on semiconductor surfaces using STM, Low Energy Electron Microscopy (LEEM), and X-ray Photoelectron Spectroscopy (XPS). The system in Chiang's laboratory

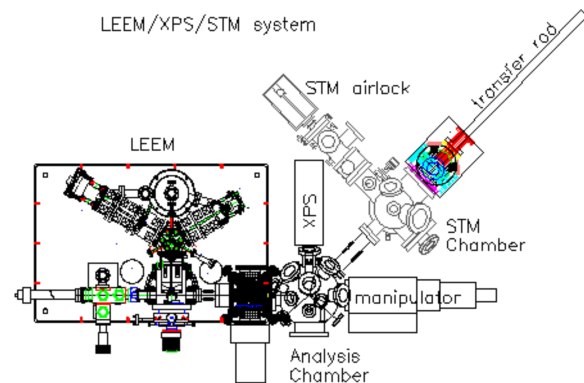


Fig 1. A schematic of the instrumentation in Prof. Chiang's lab. The LEEM was not used during this experiment, but the STM and XPS were both used for measurements.

combines these three instruments in interconnected ultra-high vacuum (UHV) chambers which allow measurements to be made by all of these techniques on the same sample without exposing the sample to contamination from air [2]. This paper concerns itself only with the STM and XPS.

This experiment investigated Pb deposited on highly polished Ge(111) crystal wafers. The sample was cleaned via cycles of Ar^+ ion sputtering and annealing. Then it was placed into the STM, where it cooled before the Pb was deposited onto it. The experiment uses the STM to investigate the formation of islands with preferred thicknesses due to quantum size effects, which have been observed previously for the system of Pb on Si(111) [3,4]. These effects were not observed on surfaces with other orientations such as Si(110), so this experiment deals with the (111) surface only.

Quantum size effects can appear in systems where physical length scales of the system in one or two dimensions are on the order of electron wavelengths. In this case, the thicknesses of the Pb islands can be considered as corresponding to the width of potential wells. Electron wavefunctions can either constructively or destructively interfere in these potential wells, resulting in stable or unstable island heights, respectively.

This experiment seeks to discern whether similar effects observed on Si(111) surfaces occur on Ge(111), a closely related superconductor, as well as to see how the effects are altered by unique characteristics of Ge crystals such as interatomic spacing. Additionally, it seeks to develop a better model for the dependence of island height and size on temperature and coverage, which contributes to the development of more robust theory describing surface interactions overall.

A. UHV system

When working on atomic scales, particles in the air such as water and dust could contaminate the sample. UHV means maintaining the system at a pressure of 10^{-10} torr. At these pressures, the time it would take for the entire surface of the sample to be contaminated goes from seconds to hours, which allows for measurements to be made before the features being observed are obscured.

Moving samples and scanners within the vacuum chambers is achieved using transfer arms for lateral movement between chambers and a claw to place the sample into the STM. These methods are sometimes precarious, and it is vital to avoid dropping the fragile sample holders inside the chambers.

Flanges on vacuum chambers are sealed with copper gaskets and tightened to 180 inch-pounds. Knife edges on the flanges cut into the gasket to obtain a tight seal. A new gasket is used each time a flange is re-sealed.

Each chamber can be isolated from the others by gate valves, which allows for the opening of one chamber without destroying vacuum in the others. Vacuum is broken in the

loading chamber any time samples or scanners need to be removed for maintenance, and in the other chambers to perform maintenance or retrieve fallen sample holders.

Restoring vacuum in one of the main chambers is a long process. The chamber must be carefully re-sealed and then pumped out by mechanical and turbo pumps. Meanwhile, the exterior is wrapped in heating tapes and aluminum foil in order to bake the chamber above the boiling point of water overnight. This serves to quickly remove the water molecules that have been absorbed into the chamber walls, which would otherwise slowly outgas and prevent the achievement of the desired low pressures. In addition, handling any components that will be placed under vacuum must be done with gloves in order to avoid contaminating them with oils, since organic compounds are notorious for degrading vacuum pressure.

The morning after the bake, titanium sublimation pumps are used to remove reactive gas particles by binding them to Ti atoms. All filaments are degassed at this stage, including ion pressure gauges. Once the pressure is sufficiently low, the ion pump is turned on, which pumps the chambers the rest of the way to the desired pressures.

To reduce mechanical vibrations during STM operation, mechanical and turbo pumps must be turned off, leaving the ion pumps to maintain the vacuum.

B. Sample holders and scanners

The sample holders are specially machined to be compatible with both the LEEM and STM. Older models are made of Mo, but newer ones are made of either Ti or stainless steel.

The sample holder has a K-type (chromel-alumel) thermocouple, which has contacts on the bottom and attaches to a ring upon which the sample sits. Ceramic insulating tubes isolate the thermocouple wires from the holder. Below the sample is a cup that houses the W filament, which also connects to a pair of contacts on the bottom of the holder. A current can be run through the filament, which causes it

to eject electrons and heat the sample for cleaning.

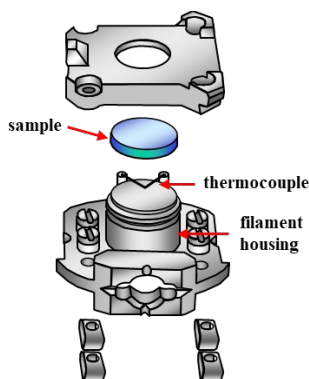


Fig 2. An exploded view of the sample holders used in the STM

The removable scanner has a piezoelectric tube to allow three-dimensional movement of the tip near the sample surface. The tungsten tip is inserted into a metal tube which is epoxied to the inside of the piezoelectric tube. The scanner is placed on top of the sample holder and additional piezoelectric tubes are used to raise and lower the scanner tripod for approaching the tip towards the sample in sub-micron steps.



Fig 3. An STM scanner. The scanners perform vertical approach and can be removed from the instrument. The orange arrow indicates the location of the tube that holds tips. The tube is connected to a peg that allows a bias voltage to be applied.

C. STM

STM is a technique for imaging surfaces which can achieve resolution on the scale of interatomic distances. The tunneling current of electrons between the atomically sharp tip and the sample surface, which are biased relative to

each other at a set voltage, is governed by the equation

$$I \propto V e^{-A\sqrt{\Phi}z}$$

where V is the bias voltage, Φ is the average work function of the tip and sample, z is the height of the tip above the sample, and A is a constant. From this relationship, it follows that the tunneling current is very sensitive to changes in the z height of the tip above the surface.

Electrons tunnel either from occupied states in the tip to unoccupied states in the sample or occupied states in the sample to unoccupied ones in the tip, depending on the sign of the bias voltage applied. Changing the sign of the voltage thus changes what is being imaged, and can result in different images if the electronic states differ. Although it is often useful to consider STM images as actual topographical representations of the surface, the image is actually a representation of the electronic orbitals of the surface.

STM can function in two ways—images can be measured either at fixed current or fixed height [5]. The STM used in this experiment uses fixed current. A feedback circuit adjusts the height up or down to maintain the designated current set point. The scanner is capable of vertical height adjustments on the scale of microns using a wedge under one leg of the scanner tripod, which is moved back and forth by a piezoelectric crystal. Successive scans of z versus x are done for each y value to create a full, topographical image.

D. XPS

X-ray photoemission spectroscopy uses Mg $K\alpha$ or Al $K\alpha$ x-rays that excite electrons in the surface, overcoming the work function and ejecting them. The electrons go through an energy analyzer which uses a voltage to select electrons with certain kinetic energies. The analyzer sweeps over a range of energies to create a spectrum. The binding energy of the

electrons can be calculated by subtracting the kinetic energy from the x-ray energy,

Energy peaks measured by XPS can be compared to tabulated values to determine the orbital and element to which they correspond. Comparing the integral area under different peaks yields a ratio that can be used to determine the relative abundance of different materials on the sample.

3. METHODS

A. Etching tips

The methods used are described in [6]. A solution of 3M KOH is placed into a special piece of glassware consisting of two cylindrical chambers connected by a tube. This apparatus is placed onto a ring stand with a gold electrode in one side. One-cm lengths of tungsten wire are trimmed and placed into a small pin vise. The wire is then immersed up to a depth of 5mm on the other side of the glassware. A lead is connected to the pin vise, and a voltage is applied which results in a current through the system, which maintained for several seconds to clean the wire. The depth is then adjusted to approximately 1-2mm and the apparatus is covered in foil to avoid disturbances of the surface of the KOH.

The voltage is applied again until the current goes to zero. The current causes an electrochemical reaction which begins to etch away the surface of the submerged wire at the level of the liquid meniscus. As the wire grows thinner, it begins to stretch under its own weight. The end of the wire eventually falls off and electrical contact is lost with the solution, leaving behind a sharp cusp.

The tip must then be rinsed in methanol and water before being observed under a microscope to check for imperfections. Etching the tip at the wrong depth can result in a tip that is too long, too short, or misshapen.

The tip wire can be annealed before etching to remove impurities and make higher quality tips that should produce better images.

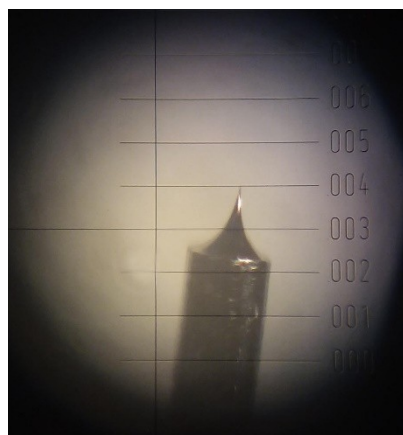


Fig 4. A finished tip seen through an optical microscope. The tick marks are spaced at $1/10^{\text{th}}$ of a millimeter. Photo taken by Andrew Kim.

B. Preparing samples

Ge(111) wafers are scored using a diamond scribe and then snapped along the score using pliers. The samples are cleaned in a ultrasonic cleaner, first in hydrogen peroxide and then in methanol to remove any organic compounds. The samples are then placed inside the sample holders and the top plate is carefully tightened.

The prepared sample holders are then placed on the loading tray which goes into the airlock chamber. The airlock must be baked for a minimum of four hours after being open to atmosphere. The tray is then loaded into the STM chamber, and the sample holder is placed onto the transfer arm and moved into the XPS chamber. The manipulator is adjusted to the cleaning position.

The cleaning process is done by cycles of sputtering the surface with Ar^+ ions, followed by annealing at 800C. In order to attain annealing temperatures, a current of 2.6 or 2.7 amps goes through the filament on the sample holder which causes the sample to heat up. Any higher current will cause the filament to burn out, so if this is insufficient to obtain the desired temperature, a high voltage bias on the sample is used to do so. A timer is used to turn on and off the high voltage at specified intervals, and the sputtering gun is left on overnight to approximate the desired cycles. The following day, two or three manual cycles are completed, in which the filament and high

voltage are turned off for sputtering and the sputtering gun is turned off for annealing. The cleaning is finished off with a 15 minute annealing.

Once cleaned, the sample is transported back to the STM chamber and inserted into the instrument.

C. Performing a scan

This experiment is run at 240K, which is achieved using a continuous flow cryostat with liquid nitrogen. The temperature is regulated by a feedback circuit attached to the thermocouple. A vacuum-insulated transfer tube and nitrogen gas pressurization is used to pump liquid nitrogen into the STM.

Cooling begins as soon as the sample cleaning is completed. The sample requires approximately one hour to reach the desired temperature. Once the sample has reached the target temperature, Pb is deposited on the surface using an evaporator. The evaporator consists of a tungsten basket containing a small ball of solid lead which is heated with a current that is calibrated to achieve deposition of 0.8-1 monolayers per second. The deposition time ranges from 15 to 45 minutes. The scanner is then placed on top of the sample. Due to the temperature difference, two hours must be allowed for thermal drift to decrease before scans can be acquired.

Vibration isolation is key to reducing noise in STM images. This is achieved in two ways. First, we use laminar flow isolators which are filled with N₂ gas and float the entire system. Second, the STM stage is suspended on springs for additional vibration isolation. Magnets are mounted close to small copper blocks so that vibrations of the springs cause eddy currents in the copper, allowing the oscillations to damp quickly.

An optical microscope is affixed to the outside of the STM and used to visually assess the distance of the tip from the sample. An electrical controller allows coarse height adjustments by moving the wedge under one leg of the scanner, until they are almost close enough to allow tunneling. It is essential to

avoid crashing the tip into the sample, which will ruin atomic sharpness of the tip. The range of motion for coarse adjustment is approximately 1.8mm. Once the tip is sufficiently close, a computer program completes the approach process, in which the wedge is moved back incrementally until a tunneling current is detected.

A software program specifically designed to run STM scans is used to translate measured height differences into a 3-D image of the surface.

D. Modeling

In order to calibrate the XPS spectra for measuring surface composition of our samples, software called Simulation of Electron Spectra for Surface Analysis (SESSA) was used [7]. Simulated XPS spectra were created for various coverages. Functions in MATLAB were then used to perform background subtraction on collected data to account for physical aberrations as well as distortion due to neighboring peaks. These curves were compared to the simulated peaks to calibrate the background subtraction parameters.

4. EXPERIMENTAL CHALLENGES

The complexity and age of the equipment led to many experimental challenges. Sample holder components such as the filament housing cup and thermocouple are incredibly fragile and require patience and precision to repair. The Ge samples are also quite brittle and can break easily while being prepared or fastened into sample holders.

The UHV chambers and apparatus require many special techniques. The pumps are relatively fragile, and procedures must be carefully followed to avoid damaging the pumps or degrading the pressure inside.

The magnetic transfer arm mechanism that moves samples from the STM to the XPS posed more mechanical difficulties. A magnetic ring on the outside of the vacuum tube aligns with and drags magnets on the inside, which are

attached to the arm itself. At the beginning of the series of experiments, we noticed extreme roughness in the transfer arm. Upon examination, we found that a washer that had lodged itself between the arm and the housing tube was dragging and impeding the motion. Even after removing the washer, we continued to struggle with roughness of the mechanism, which posed the threat of dropping sample holders. Eventually the arm stopped working entirely and had to be replaced.

Both STM scanners required repairs. In one, the tip-holding tube was replaced twice. In the other, the tip wire and ground wire had to be re-attached. For both scanners, solder rather than silver epoxy was used to affix the tip wire to the tip tube, in order to ensure stronger, more lasting electrical contacts. Testing whether repairs are successful is difficult because replacing tips or modifying the scanner necessitates its removal and then replacement into vacuum, a process which takes a minimum of four hours. It is easy to accidentally crash tips or for tips to be too far away to approach if the height calibration is off by tenths of millimeters, or if the sample being used is slightly higher or lower than usual.

Since the piezoelectric crystal responsible for the z position adjustments in the STM was beginning to fail, we removed the STM from the vacuum chamber to replace it. Although this process is time-consuming and risks damage to the system, it also allowed for more rapid testing of the repaired scanner, which led to the discovery that the replacement tube had inconsistent connections with the tip. Following this discovery, the tube was replaced once again, this time with satisfactory results.

5. RESULTS

During scanner testing, a raw image of the uncleaned Ge surface was taken (Fig. 5). This image demonstrates the importance of the cleaning process, which creates an atomically smooth surface on which to observe the behavior of Pb islands.

Several images were successfully recorded of Ge(111) after cleaning and Pb deposition (Fig

6). The large surface features appear to be Pb islands. The islands are large and disordered. Notably, the island height is on the order of hundreds of angstroms, which does not match our expectations based on the Pb on Si(111) results, which yielded islands on the order of several angstroms in height [3, 4]. This may indicate low mobility of the Pb atoms on the Ge(111) surface. More data are required along with corresponding XPS spectra to draw meaningful conclusions.

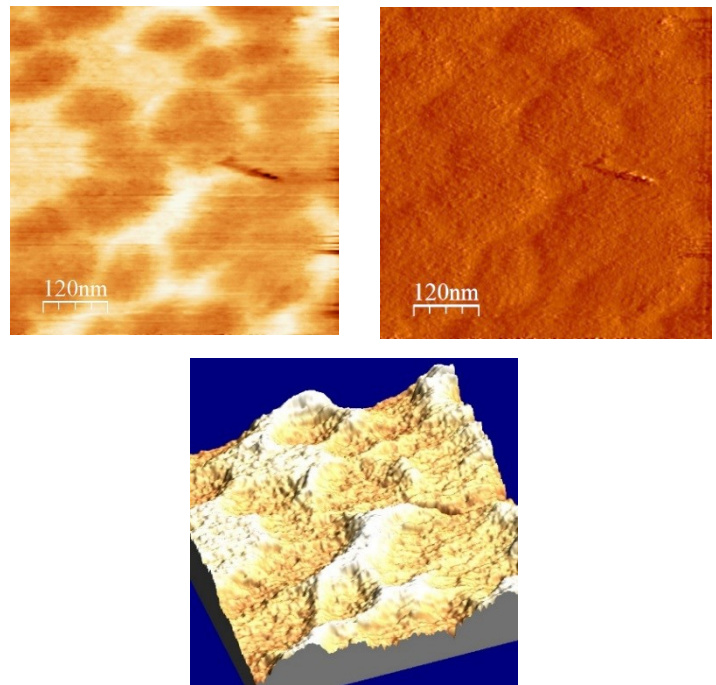


Fig 5. Topographical, derivative, and 3D rendering of uncleaned Ge(111) collected during testing of a repaired STM scanner in air. Bias voltage 2V, tunneling current 2nA. No vibration isolation or electrical shielding was used. Z height varies by 27nm.

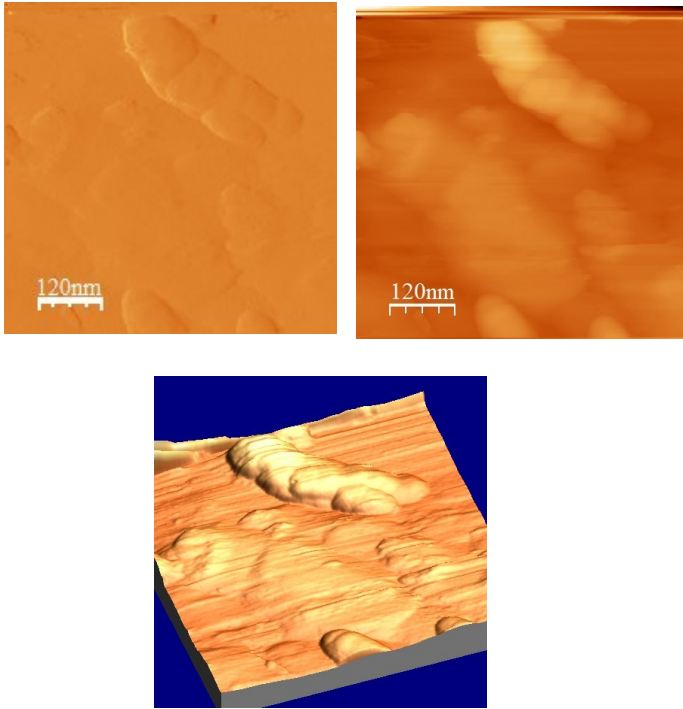


Fig 6. Topographical, derivative, and 3D rendering of Pb on a clean Ge(111) sample. Bias voltage 2V, tunneling current 2nA. Z height varies by 45nm. Images were processed using WsXM [8].

6. CONCLUSION

More work is required to calibrate the deposition rate of the Pb and resolve remaining issues with electronic noise before high quality, usable images can be collected.

When images of Pb islands on our Ge(111) sample surface are successfully collected, analysis of the data can begin. The island sizes and heights will be noted, and XPS spectra will be used to measure the Pb coverage. Measuring coverage will permit more

precise calibration of the deposition, which will in turn allow for the development of a phase diagram for the Pb/Ge(111) system.

7. ACKNOWLEDGEMENTS

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