The Influence of Arsenic on Silicon Surfaces

BY

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This Thesis is dedicated to my mother and father
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<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>ARXPS</td>
<td>angle resolved X-ray photoelectron spectroscopy</td>
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<tr>
<td>Eb</td>
<td>binding energy</td>
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<td>ESD</td>
<td>electron stimulated desorption</td>
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<td>surface core level shift</td>
</tr>
<tr>
<td>TM</td>
<td>transition metal</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>RHEED</td>
<td>reflection high energy electron diffraction</td>
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</table>
SUMMARY

Single crystal silicon surfaces are a significant research subject because of their utility in creating complex materials. The Si(112)/As surface has been discovered empirically to be a particularly suitable substrate for molecular beam epitaxy (MBE) growth of Si(112)/As/ZnTe/CdTe thin films. Since the Si(112)/As surface produces the best CdTe thin films, this work focuses specifically on clean Si(112) and arsenic-covered Si(112) surfaces. Restructuring of the clean Si(112) surface due to annealing, and the role of the As precursor monolayer on clean Si(112) for the MBE growth of Si(112)/As/ZnTe/CdTe thin films were explored, employing scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED). The arsenic monolayers were deposited on clean Si(112) surfaces under ultra high vacuum (UHV), mimicking the first two steps in the MBE growth of single crystal Si(112)/As/ZnTe/CdTe thin films. The hypothesis for this research, presented in the MBE literature, predicts that the arsenic will be covalently bonded to the edge atoms of the bulk terminated Si(112) surface and that no surface faceting will occur.

Chapter 3 presents a STM survey of Si(112) surfaces resulting from differing number, durations and temperature of annealing cycles. The structures observed on these surfaces include: 1) non-planar Si(111)-like facets running in the [1-10] direction, from above to below the Si(112) surface plane rotated 2° about the [11-1] direction; 2) a 2.05 nm periodicity in the [1-10] direction on the line where the (111) and (113) facet planes meet at the surface; 3) dual Si(111)-like hexagonal periodicities with a = 0.384 and a’ = 0.3905 nm that are matched to the surfaces; 4) a LEED image of a high temperature annealed Si(112) surface is presented with a proposed centered rectangular unit cell with a = 0.384 nm and b = 3.516 nm, and 5) long range
ordering with a superlattice with hexagonal periodicity with $a = 78.1$ nm, for the high
temperature annealed Si(112) surface.

Chapter 4 summarizes the study of the arsenic covered Si(112) surface. From the STM
images, 2.0 ± 0.05 nm wide rows in the [11-1] direction, running parallel to the [1-10] direction
on the clean annealed Si(112)/As surfaces, were observed. No faceting was observed. The dual
hexagonal periodicity used to describe the clean annealed Si(112) surface also is shown to match
well with the Si(112) arsenic covered surface. When a STM image (62.1nm × 62.1nm) of a
Si(112)/As surface is overlaid on a STM image (57.1 × 57.1 nm) of a clean high-temperature
annealed Si(112) surface, there is a strong correlation of surface features in the two images.
As a result, an alternative hypothesis to the initial hypothesis is presented. The arsenic adlayer
forms 2.0 nm rows in the [1-10] direction on the Si(112) surface and no faceting occurs. The
atoms are not lattice matched to the bulk-terminated Si(112) surface but form a moiré pattern
layer. The arsenic layer preserves the clean high temperature annealed Si(112) surface
reconstructions as the surface is cooled to room temperature. Si(111)-like nanofacets are not
observed for the room temperature Si(112)/As surface.
INTRODUCTION

1.1 **Rationale**

HgCdTe and CdTe thin films have significant advanced applications in the role of IR detectors and photovoltaics. The gold standard for producing the highest quality single crystal HgCdTe thin films for IR detection is by using lattice matched CdZnTe substrates. However, these substrates have a very high cost ($800 per cm$^2$). Over the past 15 years, a large effort by the II-VI community has led to breakthroughs using other lower cost substrate materials, such as GaAs and Si. In fact, Si substrates ($10 per cm^2$) have been found to yield high quality HgCdTe, with Si(112) as the preferred single crystal orientation. Si(112) has been shown to produce superior HgCdTe films when compared to the ubiquitous Si(111) and Si(100) substrates by molecular beam epitaxy. Although, the Si(112) surface is known as a pseudo-stable surface and tends to reconstruct when annealing, a modest amount of work has been carried out to understand this phenomena. In other words, the Si(112) surface is not well understood. It has been found that an arsenic monolayer, as the precursor layer, is necessary for high quality growth of CdTe thin films. Defects in the interface region at the surface of Si(112) substrate tend to propagate into the CdTe and, eventually, into the HgCdTe; thus, reducing their quality. Gaining insights into the processes occurring at the interface of Si(112) is of great importance. This dissertation investigates this interfacial region of the Si(112) surface, its reconstructions during annealing, and the structure of the arsenic precursor layer in the interface region.

1.2 **Single crystal silicon and surface planes**

Single crystal silicon has a diamond bulk structure. It can be cut at specific angles resulting in exposed stable surface planes. The Si(111), Si(112) and Si(113) facet planes formed
during the reconstruction of the Si(112) surface during annealing are important to this study. The bulk terminated surface structures of the Si(112) and Si(113) planes are shown in Figure 1. Due to the instability of the single and double dangling bonds produced by the triple and double coordinated surface layer silicon atoms, each of these surfaces undergoes various reconstructions during the annealing process required to produce clean Si surfaces.(1)

The Si(111)-(7×7) has the lowest surface energy of these Si surface planes, and therefore is one of the most stable Si surfaces.(1) With the proper preparation recipe, the Si(111)-(7×7) reconstruction without faceting can be produced throughout an entire sample with regularity. Due to Si(111)-(7×7) surface’s well known parameters, reproducibility, and stable behavior, it has been a surface of choice for many MBE growth processes. These qualities also make it the surface of choice in STM work to test the STM system and, particularly, to calibrate the applied volts to distance of movement for the piezo.

Si(112) is less stable as it reconstructs during annealing into nanofacets.(2) The reconstruction on Si(112) indicates clear periodicity in the [1-10] direction, but not in the [11-1] direction. The quasi-stable nature of the Si(112) surface has made it a challenge to study. In 1988, Kaplin (3) published several different LEED patterns for different annealing temperatures and, in 1995, Mochrie et.al.(4) demonstrated five different surface morphologies using X-ray scattering for a temperature range from 300 to 1400 K. Reconciling LEED analysis of the Si(112) surface, with our STM results is addressed in Chapter 3.
Figure 1. Two models of bulk-terminated silicon surface planes where a) is the bulk-terminated Si(112) surface and b) is the bulk-terminated Si(113) surface. The green silicon atoms have single dangling bonds and the red have double dangling bonds.
Si(113) has one of the lower surface energies for the higher index planes. Also, it does not easily facet into other Si planes during reconstruction when properly annealed for cleaning. The clean Si(113) surface shows a 3×2 reconstruction, although the specific atomic placement is not agreed upon in the literature.\(^5\) A comparison STM study of the nature of these clean silicon surfaces is reported by Baski et al.\(^6\) Being stable planes, both the (111) and (113) facets can often be observed by STM on the clean annealed Si(112) surface.

Although silicon surfaces have been employed for many types of thin films grown by MBE, it is clear that a given chemical system will grow differently on different surface planes. Si(112) has proved to be a useful surface for growing high quality single crystal CdTe thin films. However, there is still much to be understood about the reasons it works so well.\(^7\) With research, Si(112) has shown improved results with future potential.\(^8\) However, faceting of the Si(112) during processing for MBE growth into the Si(111) plane facets, as well as other facets, reduces the quality of the subsequently grown single crystal CdTe thin films.\(^9\) STM of both the clean annealed Si(112) and the MBE produced Si(112)/As surfaces were employed in this work to improve our understanding of MBE production of the CdTe thin films on the Si(112) substrate.
1.3 Molecular beam epitaxy and arsenic

Arsenic is used during thin film growth as an initial precursor layer at the interface between the silicon surface and the thin film which is to be grown. In 1996, arsenic was first employed as a precursor layer added to the Si(112)/CdTe MBE growth process during the initial cooling step of the cleaning anneal. The commonly proposed functions of arsenic’s role in producing quality MBE growth of CdTe thin films on Si(112) are that it acts as a surfactant and/or passivant of the initially clean Si(112) surface.(10) In its role as a surfactant, arsenic is assumed to increase the mobility of the Te adatoms on the surface, allowing them to move more freely over the surface before bonding at a lattice-matching site, and by restricting the lattice location where the Te can bond. It is also thought that arsenic might act as a passivant on the silicon surface. In this case, the As is credited with effectively passivating the surface so that impurities, which would cause a greater number of defects, are restricted from reacting with the surface. Further, a monolayer of arsenic on clean Si(112) as a precursor layer appears to be required to produce Te as the first layer of growth to produce a B face Si(112)/CdTe thin film.(11) At present there is still debate concerning arsenic’s full function, but it is agreed that a monolayer of arsenic is a necessary component of the recipe for good growth of Si/CdTe thin films, although little As has been observed incorporated into the finished thin film. This is recounted well in Chad Fulk’s PhD Thesis.(11)

A further comment must be made regarding the function of arsenic during the Si(112)/CdTe thin film MBE growth process: the deposition of arsenic might also impede nanofacet formation as described by Baski and Whitman (2) during the annealing or cleaning step of the MBE growth process. Chapter 4 discusses this hypothesis.
Arsenic monolayers are commonly produced on these Si(112) surfaces by MBE techniques. Clear reproducible LEED patterns are produced and observed for these mono-layers on the Si(111), Si(112), and Si(113) surface planes. STM images and LEED patterns of the same surfaces are compared and analyzed in Chapters 3 and 4.

1.4 **X-ray photoelectron spectroscopy (XPS)**

X-ray Photoelectron Spectroscopy (XPS) is a qualitative and quantitative chemical analysis technique used to investigate the surface of a material from 1 to 10 nm in depth. XPS can identify the elements present, their chemical and electronic states, and the empirical formula of a sample. In the case of monolayer depositions, the surface coverage can be extracted. For the systems used in this work, the XPS spectra were produced by irradiating the sample surface with a X-ray beam produced from either an Mg or an Al anode excited by a 15 kV electron beam. When a photon of X-ray radiation is absorbed by an atom in the sample it can lead to ionization of that atom causing the emission of an inner core electron. Emitted electrons are measured by an electron energy analyzer and recorded as a function of the number of emitted photoelectrons versus their kinetic energy.

The overall process can be described as follows:

\[ A + hv \rightarrow A^+ + e^- \]

Applying conservation of energy to the process leads to:

\[ E(A) + hv = E(A^+) + E(e^-) \]

where \( E(e^-) \) equals the kinetic energy (KE) of the photoelectron. In addition, a small correction is required due to the work function of the spectrometer (\( \Phi_{sp} \)) which relates the \( E_f \) to \( E_{vac} \) : 

\[ \Phi_{sp} = E_f - E_{vac} \]
Where $E_f$ is the Fermi energy level and $E_{\text{vac}}$ is the vacuum energy level.

Rearranging the equation with these considerations gives:

$$KE = hv - (E(A^+) - E(A)) - \Phi_{sp}$$

Finally, the term $(E(A^+) - E(A))$ represents the binding energy ($E_B$), which is the difference between the energy of the neutral atom and the ionized atom. The final rearrangement develops the analytically useful equation:

$$KE = hv - BE - \Phi_{sp}$$

The binding energies of the electrons are precisely dependent on the local chemical environment of the ionizing surface’s atoms as well as their elemental identity. The shifts in BE values not only identify the elements present, but with further analysis, also indicate their relative quantities and oxidation states.

1.5 **Low energy electron diffraction (LEED)**

Low energy electron diffraction is a surface analysis technique used to observe periodicity on a surface. The surface unit cell, with dimensions and angles, can be determined under UHV conditions. Faceting, reconstructions, and adsorbate order and placement on the underlying unit cell can be observed. The limit of coherence length for observable periodicity on the surface is 50.0 nm. The degree of contrast between the brightest spots and the background is indicative of the degree of order on the sampled surface. In a LEED experiment, a beam of mono-energetic electrons is directed toward the sample surface from an electron gun at a voltage set between 20 and 500 eV. A number of these electrons are elastically backscattered toward a luminescent screen. Hemispherical grids filter out the non-elastically backscattered electrons and accelerate the elastically backscattered electrons toward the luminescent screen, forming
interference patterns that are recorded as a single image by a camera. The LEED image is interpreted as a reciprocal space representation of the 2 dimensional periodicity of the sample surface. The periodic real space lattice produces LEED patterns in which the angles of the unit cell are conserved; however, the real space and reciprocal space unit cell vectors are in inverse proportion.

The basic theory of LEED is founded on the principle of wave-particle duality which allows a beam of electrons to be considered to be the same as a series of electron waves hitting the sample surface. The atoms at the surface act as point scatterers for the elastically backscattered electrons. The wavelength of these electron waves is given by the de Broglie relation:

\[ \lambda = \frac{h}{p} \]

Where \( h \) is Planks constant and \( p \) is the momentum of the electron which can be written as a function of acceleration voltage:

\[ p = (2m.e^-.V)^{1/2} \]

Where \( m \) = rest mass of electron, \( e^- \) = electronic charge, and \( V \) = acceleration voltage. The wavelength of the electron waves is dependent on the acceleration voltage of the electron gun.

\[ \lambda = \frac{h}{(2m.e^-.V)^{1/2}} \]

Voltages from 20 V to 500 V produce beam wavelengths from 0.05 to 0.25 nm, which are suitable lengths for observing atomic spacing diffraction. The inelastic mean-free path of electrons with LEED energies in to a sample is less than 1 nm, making LEED a surface-sensitive technique. Further understanding of LEED theory and its application can be found in Pendry.(13)
For this work the diffraction pattern and spot position in the LEED data were analyzed, producing qualitative information on size, symmetry, and rotational alignment of the silicon surface unit cells and the deposited arsenic layer unit cell. LEED images are an inverse space representation of the surface of periodicities on that surface of greater than 50.0 nm. Reconciling the LEED patterns observed from clean annealed Si(112) surfaces with atomically resolved techniques, such as STM, is one of the goals of this research. The process of matching of LEED observations to structures observed by STM experiments has proven to be a challenge for the Si(112) surface. To address this point, both LEED and STM observations from the same sample surface are presented in this work. This allows for comparison and reconciliation of the results produced from the use of these two analytical techniques on that same surface.

1.6 Scanning tunneling microscopy (STM)

Scanning Tunneling Microscopy is a non-optical imaging process that converts a tunneling current between an atomically sharp tip as it is scanned across a conducting or semiconducting surface into an image. It was invented and successfully demonstrated, in 1981, by Gerd Binning and Heinrich Rohrer, for which they received the 1986 Nobel Prize in Physics. (14) Under ideal tip, surface, and environmental conditions, and in a properly calibrated system, images of the electron density of the sample surface at or below sub-nanometer resolution can be obtained. With careful analysis, the researcher can utilize these electron density images to deduce the arrangement of individual atoms in the surface lattice. Therefore, STM is a powerful technique for studying and understanding conducting and semiconducting surfaces.
However, obtaining the ideal conditions for successful imaging at atomic resolution can be challenging. The tunneling current employed in STM is a quantum mechanical effect which occurs between the sample surface and the tip under an electrical potential difference.

The applied voltage difference or bias for the tunneling between the tip and a highly conducting surface can be in the 100 to 300 millivolts (mV) range. For semiconductor surfaces, with greater bandgaps, the bias can be up to 3 Volts in range. Useful currents range between .01 to 5 nanoamperes (nA). The distances between the tip and sample are on the order of a nm but may be as small as picometers (pm). For additional detail see references. (15,16)

Shown in Figure 2 is a (16.0 × 16.0 nm) region of the Si(111)-(7×7) surface. The bias is 1.9 V, the set point is 0.06 nA and the Z amplitude is 0.33 nm. The white diamond defines one unit cell for the Si(111)-(7×7) reconstruction with a = 2.688nm. Figure 3 is a STM image (20 × 20 nm) of the Si(111)-(7×7) reconstructed surface. The bias is 1.55 V and the set point is 0.01 nA. The Z amplitude is 1.0 nm. There is a double step up from blue to yellow showing three layers of the Si(111)-(7×7) surface. Images such as these are used to calibrate the STM by using the well studied distances for the Si(111)-(7×7) unit cell for calibration of the X and Y directions. The step heights or the distance between the Si(111) planes are used for calibration of the Z direction.
Figure 2. This is a STM image (16.0 × 16.0 nm) of the Si(111)-(7×7) surface. The bias is 1.9 V and the set point is 0.06 nA. The Z amplitude is 0.33 nm. The white diamond outlines the Si(111)-(7×7) hexagonal unit cell with a = 2.688 nm.
Figure 3. This is a STM image (20 × 20 nm) of the Si(111)-(7×7) reconstructed surface. The bias is 1.55 V and the set point is 0.01 nA. The Z amplitude is 1.0 nm. There is a double step up from blue to yellow showing three layers of the Si(111)-(7×7) surface.
1.7 **Sample surface preparation.**

High quality STM imaging requires both a clean and a smooth surface. A clean but rough surface produces poor results for two reasons. First is the experimental process by which the tip is moved across the surface. In topographic mode the tip is maintained at a specific tunneling current by varying the applied voltage on the scanning electric crystal (“piezo”). This results in the tip moving closer or farther away from the surface along the Z-Axis. The feedback used to maintain the “set point” current is not instantaneous and the tip will oscillate. Filters are used helping to stabilize the tunneling signal and, when carefully applied, produce images with atomic resolution. The greater the change in Z with respect to the change in X or Y the more difficult it is to observe smaller variations in the surface.

The second reason for poor results is a contaminated sample surface. Even when a “clear” image is produced by a contaminated surface, the relationship of that section of the surface to the experimentally observed surface remains unclear. A well prepared surface is critical to obtaining useful images by STM. Annealing to high temperatures under UHV to remove surface contaminations and smooth the surface is necessary for STM work.

STM tips are required to be clean and atomically “sharp” in order to obtain atomic resolution. For these experiments, the tips are tungsten metal. The procedure for making tips in our lab is described in Rasdip Singh’s thesis.(17) The polarity of the bias affects the direction of the electron flow. A sample with an applied negative bias will cause electrons to tunnel from the filled states in the sample surface to the empty states of the tip material. Alternatively, a positive sample bias will produce a tunneling current that causes the electrons to leave the filled states of the tungsten tip and to be collected at the empty states of the sample surface. The images produced from the two biases on the same surface probe different states and provide potentially useful complementary information for understanding the surface structure.(18)
2. **EXPERIMENTAL DETAILS**

The experimental design for this work is constrained by several factors. The use of different growth and analysis chambers conflict with the requirements for *in situ* surface analysis by LEED, XPS and STM. There are three main constraints for successful surface analysis for this study: UHV conditions, MBE recipe requirements, and experimental requirements. It would be advantageous in certain respects to have a surface analysis chamber connected *in situ* with the MBE growth chamber. The unavailability of this arrangement was addressed by adding a UHV connected arsenic deposition chamber to our analytical chamber, allowing improved conformity to the MBE growth processes used to produce Si(112)/CdTe thin films. For many other analytical studies, samples may be produced and then transferred for further analysis to the analysis chamber under non-UHV conditions with tolerable sample degradation. In contrast, surface science analysis is concerned with the clean, prepared surface layer which is unaltered by the deposition of ambient atoms or compounds on the clean surface. A monolayer of impurities forms on a sample’s surface within 1 second for an ambient pressure of $10^{-6}$ Torr.\(^{(17)}\) The contamination of the surface destroys much useful information when surface analytical techniques are applied to an impurity covered sample surface. Therefore, all samples studied must be held under UHV at all times for the maximum amount of experimental data to be obtained.

Highest quality MBE growth for CdTe thin films on Si(112) requires adherence to a strict recipe under UHV conditions. The process is continuous and cannot be halted, even briefly, without compromising the quality of the thin film growth. Si(112) wafers were obtained from the manufacture, Virginia Semiconductor, and employed as received at the beginning of this procedure. After a modified RCA process (Appendix A), Si(112) wafer samples are initially
annealed under UHV conditions (<10^{-9} Torr) only once to approximately 950°C following the wafer’s introduction to the MBE chamber. Under As_4 flux it is cooled immediately at a rate of 1°C/s to 2°C/s to 360°C, then heated to 400°C for 5 minutes under continued As_4 flux creating an As monolayer on the surface of the Si(112) wafer. The growth then follows with deposition of a ZnTe buffer layer, added to help reduce strain due to the lattice mismatch (19%) between Si(112) and CdTe single crystal layers. This dissertation concerns the growth processes up to and including the deposition of the As monolayer. To this end a small MBE chamber for depositing As on silicon wafer samples was designed, built, and added to the surface analysis chamber in our laboratory.

Successful STM imaging has rigorous requirements beyond a sample surface prepared to particular specifications. They include temperature stability, quality of the tip and sample, vibration isolation, and proper sample mounting for analysis. These needs also introduce further restrictions on how well STM analysis can be applied to the study of the surface of Si(112) with an arsenic monolayer. In meeting the requirements for useful STM results from these experiments the requirements for successful LEED and XPS analysis were also satisfied. Direct analysis by LEED, XPS, and STM of the MBE grown monolayer of As on Si(112) by the University of Illinois Microphysics Laboratory (MPL) was not practical. By creative experimental design, implementation, and analysis, a significantly improved understanding of the physical processes involved in the first two steps of MBE thin film growth for Si(112)/CdTe became possible. The unique experimental aspects involved are described below.
2.1 **Ultrahigh vacuum (UHV) surface analysis chamber**

The UHV surface analysis chamber has been described previously in detail.\(^\text{(19,20)}\) There are six components of the system used for these experiments: UHV mechanics, e-beam heater, sample holder and transfer system, LEED, STM and XPS. UHV pressure of less than \(2.0 \times 10^{-10}\) Torr was maintained during the experiments. It was routinely held below \(1.0 \times 10^{-10}\) Torr during analysis. A Leybold roughing pump in series with a 150 l/s turbo pump along with a 230 l/s ion pump and Ti-ball sublimation pump maintained the base pressure. The lower the base pressure of the chamber, the greater time was available for analysis. The importance of maintaining the low base pressures for these experiments is well described in Rasdip Singh’s Ph.D thesis.\(^\text{(17)}\)

The LEED instrument was built by Princeton Research Instruments, model RVL 8-120. The XPS system was built by VG Scientific with a CLAM 100 hemispherical analyzer. Finally the STM is a MacAllister Technical Services product, Model 525DT. The surface analysis chamber is well described in Craig Perkin’s Ph.D thesis.\(^\text{(21)}\) **Figure 4** (a) is a diagram of the analysis chamber with the addition of the arsenic deposition chamber. The photographs in **Figure 4** (b) are of the deposition chamber and analysis chamber.
Figure 4. The apparatus, a) is a diagram of the surface analysis chamber used for this work. The images in b) are photographs of the analysis chamber.
2.2 Preparation chamber

Analyzing a surface as prepared during MBE growth is key to these experiments. Exposure to air or pressures of greater than $10^{-8}$ Torr does not allow enough time for sample transfer and surface analysis before surface contamination destroys the sample. A 2 liter preparation chamber was designed, built, and added to the UHV surface analysis chamber. The preparation chamber is a separate UHV capable system that can be employed separately from the main analysis chamber. Samples grown by MBE can be produced in the preparation chamber and transferred immediately for study under UHV conditions to the analysis chamber.

The volume of this chamber is smaller by a factor of ten than the MBE chambers used by the Microphysics Laboratory at UIC, posing certain difficulties. However, after bake out and during annealing and arsenic deposition, it was possible to maintain a base pressure below $2.0 \times 10^{-10}$ Torr. A temperature control system, measurement system, and custom arsenic source, the critical components for mimicking MBE growth, were designed, built, and calibrated. Experimentally, it was possible to mimic the initial steps of CdTe thin film growth on Si(112) up to and including the deposition of a monolayer of arsenic on the clean annealed Si(112) surface.

Samples of silicon wafers were cleaned by the modified RCA process (Appendix A) and introduced to the analysis chamber before bake out of the preparation chamber. The preparation chamber was then baked out to a base pressure of less than $2.0 \times 10^{-9}$ Torr. A single sample was transferred from the analysis chamber to the preparation chamber and loaded on the electron beam heater. The preparation chamber pressure was reduced further ($3 \times 10^{-10}$ Torr) by cooling an area ($100 \text{ cm}^2$) of the chamber’s top side with a liquid nitrogen filled reservoir. The smaller volume of the preparation chamber relative to the volume of conventional MBE growth chambers caused out gassing of the sample and chamber during heating to adversely affect the
pressure. This increase in base pressure was counteracted successfully with an external liquid nitrogen “cryo-cooler”. The cryo-cooler was a 250 ml container fashioned from Al foil and fitted to the top exposed outer surface of the deposition chamber. The area of contact with the deposition chamber’s surface was 200 cm². 100 ml of liquid nitrogen was added to the container and maintained during the annealing and deposition of arsenic, resulting in $3 \times 10^{-10}$ Torr base pressures in the preparation chamber.

2.3 **Electron bombardment heater**

The sample is heated from the back in both the analysis and preparation chambers with an electron bombardment heater (e-beam heater). In conventional MBE the silicon wafers are heated from the back by radiant heaters. The e-beam heaters in our chambers have the potential for much greater heating and cooling rates ($20^\circ C/s$) than the radiant heater can achieve. Cooling and heating rates (~ $2^\circ C/sec$) for the MBE recipe were used for these experiments. Careful design and construction of the e-beam heater in the chambers is critical to successful sample preparation and analysis. Ideally, the sample should be heated uniformly ($\pm 5^\circ C$) 3 mm from the center. This was best achieved with an e’-beam filament coiled in a flat disk parallel to the sample surface in comparison to an e’-beam filament coiled in a cylinder. Considerable time and effort was required for improving the design and function of the e’-beam heaters in both chambers.\(^{(22)}\)
2.4 Pyrometer

In the preparation chamber the temperature of the sample was monitored by an Omega non-contact infrared pyrometer, Model OS554-MA4, through a CaF$_2$ window (range -18° to 1370° ± 2°C). The pyrometer was calibrated with a K type thermocouple resting on a silicon sample under UHV conditions. The accuracy of the temperature measurement for this system is ± 7°C.

2.5 Arsenic Source

Deposition of arsenic onto the Si surface in the preparation chamber was accomplished by a small Knudsen cell (22) designed and constructed in our laboratory. (Figure 5) The arsenic source included: a Ta shield and shutter system operated by the wobble stick, a K-type thermocouple mounted on the shield, and a basket-shaped Ta filament for heating and cradling the arsenic metal. The heating filament of the Knudsen cell was powered by a 5 watt power AC supply. Figure 6 is an example of an XPS experiment on Si(112)/As, 30 minutes after deposition in the preparation chamber. Near monolayer coverage is indicated by the As on the Si(112) (Figure 6 ) as described by Fulk et. al. (23) with no observable carbon or oxygen contamination.

Control of the MBE system used by the Microphysics Laboratory is programmed into a computer, which runs the deposition process. All controls for the preparation chamber are manually adjusted. Normally, sample preparation for surface conditioning would include 3 to 6 anneals of the silicon surfaces for STM studies. With calibration and practice, careful monitoring of the time, the temperatures, and the pressures, it was found that the repeated annealing is necessary to produce a surface clean and smooth enough for quality STM imaging. The MPL recipe was mimicked with satisfactory results as indicated by XPS, LEED, and STM.
Figure 5. The drawing is a diagram of the lab-designed and constructed arsenic source.
Figure 6. Representative results of XPS experiments for Si(112)/As surfaces produced in our preparation chamber.
Remarkably, the arsenic monolayers on Si(112) were produced with a single annealing step followed by an arsenic deposition step resulting in a sample surface suitable for high quality STM images from a one step process \textit{in situ}. Consideration of this result sheds important light on the role of the arsenic monolayer as a precursor layer for quality thin film growth of CdTe on Si(112). Commonly, it is necessary to flash to $1100^\circ$C three to four times to successfully anneal a Si(112) surface for quality STM imaging. Arsenic evidently assists the annealing process.
3. **THE CLEAN ANNEALED SILICON (112) SURFACE**

3.1 **Introduction**

The Si(112) surface is a high energy surface relative to Si(111). Si(112) will reconstruct and facet during the surface preparation procedures used under UHV to produce a silicon surface for quality MBE growth. The cleaning protocol includes a RCA pretreatment step (Appendix A) and an annealing step.(24) The RCA process removes the oxide and impurity surface layers native to the supplied Si wafers and deposits a ‘protective’ layer of SiO$_2$. In the second step, the wafer is placed under UHV conditions and annealed to remove the SiO$_2$ surface layer and smooth the surface, exposing the clean, reconstructed Si surface. During the cleaning anneal, the maximum temperature and the rates of heating and cooling are monitored carefully and adjusted to maximize removal of the oxide layer, while minimizing the amount of faceting, reconstruction and relaxation of the sample surface. These processes occur concurrently under kinetic control, each at a rate increasing with increasing temperature. To produce a wafer with a Si(112) surface, the bulk crystal of silicon is cut along a plane whose vector is perpendicular both to the [1-10] and [11-1] directions, and tilted 19.5° from the Si(111) plane. An ideal cut, requiring no restructuring, results in a perfectly bulk-terminated Si(112) surface without faceting steps in the [11-1] direction. The Si(112)1×1 unit cell is rectangular with cell constants, $a = 0.384$ nm in the [1-10] direction and $b = 0.941$ nm in the [11-1] direction. The Si(112) plane is tilted from the Si(111) plane by 19.5°. There are 3 locations available for bonding in the [11-1] direction of the unit cell: top, terrace, and edge atoms. Both the top and the terrace locations have single dangling bonds and produce a Si(111)-like terrace 0.887 nm wide bounded by a step edge atom 0.314 nm high with double dangling bonds.(3) In approaching the question of the genesis of the surface structure of a single crystal plane, applying the model of the bulk-terminated surface is a useful
starting point. However, use of this model does not allow for consideration of the overall surface energy when restructuring and faceting occur on the single crystal surface at the atomic level. The rearrangements of the bulk terminated silicon surfaces are well documented.\(^{(25)}\)

**Figure 7** is a series of three computer generated (Cerius2) models of the Si(112) surface. **Figure 7**a) is a ball and stick model of the bulk terminated Si(112)-(1×1) surface. The green circles represent the edge atoms with double dangling bonds and the red circles represent the terrace and trench atoms with single dangling bonds. The blue rectangle is the (1×1) unit cell, 0.384 × 0.94 nm. Shown in **Figure 7** b) is a ball and stick model of a possible reconstruction of the Si(112)-(1×2) surface. It consists of a Si(113) facet with 2 Si(113) units and a Si(111) facet with 2 Si(111) units in the [11-1] direction. The blue circles are edge atoms with double dangling bonds and the yellow circles have a single dangling bond. The gray rectangle represents the Si(112)-(1×2) (0.384 × 1.88 nm) reconstructed unit cell. **Figure 7** c) is a ball and stick model of a possible reconstruction of the Si(112)-(2×2) surface. It consists of a Si(113) facet with 2 Si(113) units and a Si(111) facet with 2 Si(111) units in the [11-1] direction. The blue circles are edge atoms dimerized (blue bond) with a single dangling bond and the yellow circles have a single dangling bond. The black rectangle represents the Si(112)-(2×2) (0.768 × 1.88 nm) reconstructed unit cell.
Figure 7. Panel a) is a ball and stick model of the bulk terminated Si(112)-(1×1) surface. The green circles represent the edge atoms with double dangling bonds and the red circles represent the terrace and trench atoms with single dangling bonds. The blue rectangle is the (1×1) unit cell, 0.384 × 0.94 nm. Panel b) is a ball and stick model of a possible reconstruction of the Si(112)-(1×2) surface. It consists of a Si(113) facet with 2 Si(113) units and a Si(111) facet with 2 Si(111) units in the [11-1] direction. The blue circles are edge atoms with double dangling bonds and the yellow circles have a single dangling bond. The gray rectangle represents the Si(112)-(1×2) (0.384 × 1.88 nm) reconstructed unit cell. Panel c) is a ball and stick model of a possible reconstruction of the Si(112)-(2×2) surface. It consists of a Si(113) facet with 2 Si(113) units and a Si(111) facet with 2 Si(111) units in the [11-1] direction. The blue circles are edge atoms dimerized (blue bond) with a single dangling bond and the yellow circles have a single dangling bond. The black rectangle represents the Si(112)-(2×2) (0.768 × 1.88 nm) reconstructed unit cell.
The supplied silicon single crystal wafers are precut to the chosen plane, polished, and cleaned. Oxygen from the ambient atmosphere combines with the Si at the surface to form a (200 nm) thick layer of silicon oxide. Trace impurities are also present on the surface and need to be removed. In the 1970’s, a process was developed by RCA’s researchers which cleans Si wafers, removing surface impurities and follows with the deposition of a thinner (50 nm) SiO₂ passive layer on the surface before annealing. (24) Even trace amounts of impurities can have a major effect on the quality of the clean surface and therefore must be removed for good quality MBE growth. Variations on this chemical cleaning process have been studied by Chad Fulk and reported in his PhD thesis. (11) In that research work all Si surfaces were first cleaned with the modified process described in Appendix A, adapted from the original RCA process. In practice, the process to produce single crystal plane surfaces is not perfect, but the angle at which the wafer is cut must be chosen to be within ± 1° of the nominal surface to meet the Semiconductor Equipment and Material Industry Standards Specifications for tolerances. However, a ± 0.1° tolerance can be achieved by wafer producers. (26) The Si(112) samples used for this study have reported deviations of ±2° in the [1-10] direction.

Further issues that impact the variations in the wafer surface are warping of the surface caused by the saw cut and the subsequent polishing procedures. (27) This small variation in local regions on the wafer surface has the potential to affect the quality of the single crystal surface and therefore the MBE thin film growth. Annealing permits the surface energy to relax to a lower energy state. The two processes involved in surface relaxation are faceting and reconstruction. (25) For this discussion of the images shown in this study there are three planes that need to be distinguished. First is the ideal bulk terminated single crystal Si(112) surface shown in Figure 1, a). The second is the cut and polished Si(112) surface plane, designated as
Si(112)\textsubscript{cp}. The last plane is the Si(112) terraces which will be referred to as Si(112)\textsubscript{terrace} which are used to plane level the images to near the ideal plane. The pseudo stable nature of the Si(112) surface makes identifying the ideal Si(112) surface plane exactly from the STM images after annealing a challenge.

Lower index surfaces, including Si(111), Si(110), and Si(001), have the lowest surface energies (28) of all silicon surfaces, yet even on these surfaces, restructuring is observed routinely after annealing. At annealing temperatures, the surface undergoes reconstruction and faceting. The final surface produced is dependent on several variables; the rate of heating to the maximum temperature, the duration of the annealing time at maximum temperature, and the rate of cooling to room temperature.

The overall surface energy of the sample will be reduced during the annealing step. (29) The reconstruction process of a surface without any significant faceting has relatively fast kinetics and small surface energy differences. Thus, in the case of Si(111)-(7\times7), transitioning to Si(111)-(1\times1) can be reversed easily by annealing. (30) On the other hand, faceting occurs by mass transport of a relatively greater number of atoms and over longer distances across the surface with slower kinetics in comparison with the reconstruction processes. Faceting allows the surface to rearrange into a collection of lower energy facets with a lower average surface energy than that of the original cut surface. If the change in energy of the surface and/or the amount of mass transport is small for the transition from one restructuring to another it may be reversible by annealing. When annealing clean Si(112), there is a relatively large amount of mass transport between surface states. This process is irreversible within the constraints of the experimental design for this work, since the design is constrained by the limitations of MBE growth procedures and processes.
Clearly, a carefully controlled process must be implemented to yield high quality MBE growth of a CdTe thin film on Si(112). The difficulty with this growth is indicated by a low (10\%) success rate for producing acceptable quality for CdTe thin films on Si(112), even for production size dedicated growth chambers(31) and full width half maximum value of 72 arcsec for X-ray rocking curves.

Although the amount of restructuring which Si(112) undergoes during annealing is not significantly greater than that of the lower index surfaces, there is greater faceting and, therefore, greater mass transport.(32) Ultra High Vacuum (UHV) faceting studies of Si(111) show only (111), (110), (100), and, occasionally, (113) planes.(3) Evidence indicates that an annealed Si surface does not naturally yield detectable Si (112) facets and theoretically Si(112) is expected to be thermodynamically unstable.(33)

As presented earlier, annealing is necessary for MBE growth to remove the surface oxides produced during the RCA process. In addition, annealing reduces the roughness of the surface caused by polishing and etching. An unfortunate side effect of annealing the Si(112) surface, from a MBE point of view, is that it causes the surface to facet. One facet, observable by Reflection High Energy Electron Diffraction (RHEED), produced during annealing of the Si(112) surface is the Si(111) like plane. Si(111) is a poor surface for single crystal MBE growth of CdTe due to twinning when compared to Si(112).(34) If the Si(111) facet planes are large enough to be observed by RHEED during the annealing, further growth is terminated and that wafer is discarded. (35)

As the first UHV step in the CdTe thin film MBE growth process, this chapter describes the faceting of Si(112) during the annealing process to obtain a clean Si(112) surface. Baski’s STM work has demonstrated both the local reconstruction and nanofaceting on the annealed
clean Si(112)$_{cp}$ surface. LEED studies of clean Si(112) have been reported in reference (3). This is a complex surface which is difficult to reproduce consistently. Figure 8 is a LEED pattern produced by a clean annealed Si(112) surface at taken at a beam energy of 57.8 eV showing the 2×2 reconstruction. The nanofaceting produces a Si(111) plane 19° from the Si(112) surface that is one 7×7 unit cell wide with a second surface of mixed faceting (12-16 nm) returning the surface to the 112 plane. LEED analysis of annealed silicon (112) surfaces shows a 1×2 unit. Most results from this work agree with the previous LEED and STM results on clean Si(112), Baski and Whitman.(2) However, the results from this work also show further faceting and reconstruction of the surface after longer annealing. Surface treatments for the images in relevant figures are stated in Table 1.
Figure 8. A photograph of the LEED pattern produced by a clean annealed Si(112) surface taken at a beam energy of 57.8 eV.
<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Surface Preparation /Annealing Time</th>
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<tbody>
<tr>
<td>9 – 19,23</td>
<td>Modified RCA</td>
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<tr>
<td></td>
<td>Four separate flash anneals to 1160°C</td>
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<td>20-21.24</td>
<td>Modified RCA</td>
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<td>Modified RCA</td>
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<td></td>
<td>Annealed to 1200°C C for 24 hours</td>
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Table 1. Surface preparation and annealing procedure for the figures listed.
3.2 **Initial Anneals: Four Flash Anneals to 1160°C**

*Figure 9* is an STM image of a clean Si(112)$_{cp}$ surface after RCA pretreatment and four separate flash anneals to 1160°C. The bias was +1.8 Volts with a set point of 0.1 nA and image size of 41.0 nm × 39.2 nm. In this image there are four significant features produced by the reconstruction and faceting of the Si(112)$_{cp}$ surface during annealing to be noted. The first feature (Box 1) is a region of the reconstructed Si(112)-2×1 surface as described in the literature. The second (Box 2) has an outlined Si(111)-(7×7) reconstruction. The third feature, (*Figure 9* profiles a and b) shown in *Figure 10* a and b, demonstrates the angles of the faceting in the [11-1] direction with respect to the Si(112) surface. Finally, the fourth, (*Figure 9* profiles c and d) shown in *Figure 10* c, highlights the 2.4 ± 0.5 degree slope in the [1-10] direction of the top of the Si(111)-(7×7) facet with respect to the Si(112)$_{cp}$ surface.

Feature 1 from *Figure 9* is an area of a non-faceted, but reconstructed, Si(112)$_{cp}$ plane. The observable rows running in the [1-10] direction for this area are usually separated, in the [11-1] direction by 0.941 nm and the period of the corrugation in the [1-10] direction for these same rows is 0.384 nm, which are the bulk terminated unit cell constants shown in *Figure 7* a) There is a row in the [1-10] direction, running just above the upper boundary of the highlighted area with a period of corrugation width of 0.77 nm, indicating that these are the dimerized 2-fold coordinated edge atoms from the bulk terminated unit cell, compatible with the 2×1 unit cell. The basis for the clean Si(112) 2×1 reconstruction shown by LEED is not obvious from this image. This dimerized row like feature can be observed at a number of locations in this image and appears to be the seeding row for the base of the Si(111)-(7×7) faceting.
Figure 9. A STM image (41.0nm × 39.2 nm) of a clean Si(112) surface after RCA pretreatment and four separate flash anneals to 1160°C. The bias was +1.8 V and a set point of 0.1 nA.
Feature 2 from Figure 9 displays a Si(111)-(7×7) unit cell overlaid on the Si(111)-like facet. Si(111)-like facet planes are in various stages of formation on this surface. These Si(111) planes run parallel to the [1-10] direction. The two larger Si(111) planes clearly demonstrate two significant angles relative to the original Si(112)$_{cp}$ surface. The first angle, 19.5° (Figure 10, profiles a and b) which is expected, is that angle of the Si(111) plane with respect to the Si(112) surface. For a given Si(111)-like facet, the widths of these are constant in the [11-1] direction. Two sides of the unit cell are parallel to the [1-10] direction. However, the width of separate facets can vary.

Figure 10, profiles (a) and (b), marked as (a)-(a’) and (b)-(b’) in Figure 9, display the angles of the Si(111) and its opposite facet (that which slopes back to the Si(112) plane) relative to the Si(112) plane. As it is necessary for the combination of the angles and facet widths of the two opposite facets to return to the Si(112)$_{cp}$ plane, profile Figure 10 (a) shows a Si(111)-like facet and profile Figure 10 (b) shows the opposite facet. In both cases, above and below the Si(112)$_{cp}$ surface, the opposite facets are at commonly observed Si surface faceting plane angles. With careful inspection of the image one will observe that the two larger Si(111) facet planes are not planar with respect to the Si(112)$_{cp}$ surface regions in this image. Observing the profile one sees that the second angle of significance is the angle (2.4 ± 0.5°) (Figure 10 c) between the top row of the Si(111) plane running in the [1-10] direction, which is profile (d-d’) in Figure 9, and that of the rows of the original Si(112)$_{cp}$ surface shown in profile (c-c’) from Figure 9 running in the [1-10] direction.
Figure 10. The profile curves from Figure 9 are shown. a) is the profile a-a’, b) is the profile b-b’ and c) is the profile c-c’.
Approximately half of each of the Si(111) facets are below the plane of the original Si(112)$_{cp}$ surface and half are above that plane. This results in a Si(111) plane of constant width, running in the [1-10] direction from the right of the image above the Si(112)$_{cp}$ surface down into the Si(112)$_{cp}$ surface on the left of the image. It can be produced only by significant amounts of mass transport of the silicon atoms from their initial positions on or below the Si(112)$_{cp}$ surface to above the initial Si(112)$_{cp}$ surface plane as the Si surface is the only source of Si atoms in these experiments. According to Williams (36), the reduction of relative surface energies of this reconstruction is the driving force for faceting.

Figure 11 is a rotated 3-D view of Figure 9 for a clearer display of the 2° off the [1-10] direction of the edges of the Si(111)-(7×7) facet planes and the original Si(112)$_{cp}$ surface plane. The tolerance of the wafers used for these experiments is ± 2° in the [1-10] direction. If the actual wafer were cut at the extreme of the tolerance, the cut and polished surface would be 2° off in the [1-10] direction of the bulk single crystal. As well, this image could be of a local surface region that is off 2° in the [1-10] direction. In either case, many aspects of the resulting observed reconstruction can be explained by assuming that the 2° off the [1-10] direction was caused by error in the production processes that produced the original Si(112) wafer.
Figure 11. This figure is a 3-D perspective of the STM image in Figure 9. The Z-scale has been multiplied by a factor of 10 to enhance the visual effect of the Si (111)-like nanofacets being 2° off the cut and polished Si(112) surface in the [1-10] direction. This image also shows the non-planar nature of the Si(111)-like facets. The red line a) is parallel to the [1-10] direction and the green line b) is 2° off the (112) plane the rotated about the [11-1] direction in the [1-10] direction.
Of note, these Si(111) type nanofacets are not perfectly planar in the [11-1] direction. If one considers the point at which the top row of these planes meet the surface planes, there is clearly a slight twist (approximately 2°) to the Si(111) plane. This image also helps illustrate the ways surface stresses can be relieved by reconstruction and faceting on a surface. Figure 12 shows the Si(111)-(7×7) reconstructed facets with the top row, showing a dislocation of 1.4 ± 0.1 nm relative to the Si(112) plane at point A along the [11-1] direction. The Si(111)-(7×7) facet plane in the middle clearly shows that twist in the plane as it meets the surface as well as a distinct break with different morphology on the right.
Figure 12. A STM image ($41.0\text{nm} \times 39.2\text{ nm}$) is shown for a Si(112) surface after four separate flash anneals to $1160^\circ\text{C}$. Area 1 is a small terminal facet, $2.5 \times 2.5\text{ nm}$. Area 2 shows the angle ($\sim 10^\circ$) between top ridge of the Si(111)-like facet (a) and the limit of the deposited atoms of Si on the opposite facet. The bias $= 1.8\text{ Volts}$ and the set point $= 0.1\text{ nA}$. 
Clearly these Si(111)-(7×7) facets maintain their (7×7) like reconstruction, although they are not perfectly planar. With regard to the [11-1] direction, when the Si(111)-(7×7) facets are above the Si(112) plane, they appear slightly convex and when below the Si(112) plane, they are slightly concave. The Si(111)-like faceting process of Si(112) appears to be complicated and is not well characterized at the present time.

The portions of the Si(111)-(7×7)-like facets, where the ridge line is above the Si(112)$_{cp}$ plane, run 2.0 ± 0.4\degree to the Si(112) rows in the [1-10] direction. The width of the facets is constant for a given Si(111)-like facet in the [1-10] direction. Two sides of the unit cell are parallel to the [1-10] direction. However, the width of individual facets varies from 1.5 nm across a Si(111)-(5×5) to 2.1 nm for larger Si(111)-(7×7) facets. The Si(111)-(7×7)-like facets are 19.5 ± 0.5\degree from the Si(112) plane, as observed by Baski.(2)

From Figure 12 Area 2, the width of deposited atoms, Area 2 b), in the [11-1] direction increases proportionally with the height of the ridge line, Area 2 a), of the Si(111)-like facet above the Si(112)$_{cp}$ plane as shown by the white arrows in Area 2. Area 1 shows a small terminal facet. In this image the Si(111)-like facet’s end shifts in the [-1-11] direction 1.4 ± 0.1 nm and continues with a second Si(111)-like facet in the [1-10] direction. At the point of dislocation, the top of the Si(111)-like facet is level with the Si(112)$_{cp}$ plane and the bottom of the Si(111)-like facet is below the Si(112) plane.

Figure 13 is a zoomed image of a row termination facet. The image shows a corrugated facet with rows of large features at an off angle (approximately 8\degree) to both the [1-10] and [11-1] planes. These features are comprised of rows of 1.5 nm diameter structures. These structures are repeated in one direction at 2 nm and are stepped in height in the perpendicular direction, making the feature by the terminal facet 4 nm in height. Beyond this description of lengths and
Figure 13. A STM image of a Si(112) surface after four separate flash anneals to 1160 °C. Inset A is a zoom (12.1 × 12.1 nm) of the terminal facet. The bias = 1.8 V and the set point = 0.05 nA.
angle measurements, the exact crystal structure and the relationship to the underlying silicon single crystal structure is unclear. However, to suggest that this image depicts a low average surface energy structure is reasonable. **Figure 13**, inset A is a 3D view of the terminal facet. This image displays the facet with more clarity. This terminal facet is pseudo periodic. The 2.0 nm wide rows composed of 1.5 nm features run approximately 60° to the [1-10] direction. Also notice the Si(111)-(7×7)-like facet (grey tones) in the lower left of the insert.

**Figures (14-18)** are additional images and profiles of the terminal facet or step region. **Figure 14** shows 3D perspectives of Figure 14, inset A, from different views with the Z amplitude enhanced. Panel a) is a view down the [1-10] direction or normal to the (1-10) plane. Panel b) is a view still parallel to the [1-10] direction but rotated about the [11-1] direction toward the [112] direction or above the (112) plane. The yellow arrows represent two slopes of the Si(111) facets that differ by 2°. The lower arrow has a real slope (before Z amplitude enhancement) in the [11-1] direction of 21°. The higher arrow has a real slope in the [11-1] direction of 23°. Panel c) is a view down the [112] direction or normal to the (112) plane.

**Figure 15** is the image from **Figure 13** after Si(112) terrace leveling for slopes shown in **Figure 16** where the yellow profile is in the [1-10] direction (yellow line, and **Figure 16** b)) and the black profile is in the [11-1] direction (black line and **Figure 16** a)). In **Figure 16**, Panel a) is the black line profile in the [1-10] direction from **Figure 15**. The slope between the marked points is 8.3°. Panel b) is the yellow line profile in the [11-1] direction from **Figure 15**. The slope between the marked points is 8.5°. **Figure 17** shows a zoomed image (27.4 × 27.4 nm) leveled to the facet steps of the terminal facet from **Figure 13**. Two hexagonal periodicities are overlaid. The first is a Si(111)-like (4×4), with a_{4×4} = 1.536 nm. The second is a Si(111)-like with a =0.384 nm. The profile (green line) is perpendicular to the step edges. The crystallographic
Figure 14. This figure shows 3D perspectives of Figure 13, inset A, from different views with the Z amplitude enhanced. Panel a) is a view down the [1-10] direction or normal to the (1-10) plane. Panel b) is a view parallel to the [1-10] direction but rotated about the [11-1] direction toward the [112] direction or above the (112) plane. The yellow arrows represent two slopes of the Si(111) facets which differ by 2°. The lower positioned arrow has a real slope (before Z amplitude enhancement) in the [11-1] direction of 21°. The higher positioned arrow has a real slope in the [11-1] direction of 23°. Panel c) is a view down the [112] direction or normal to the (112) plane.
Figure 15. The image from Figure 13 after Si(112) terrace leveling for slopes in the [1-10] direction (yellow line) and in the [11-1] direction (black line).
Figure 16. Panel a) is the black line profile in the [1-10] direction from Figure 15. The slope between the marked points is 8.3°. Panel b) is the yellow line profile in the [11-1] direction from Figure 15. The slope between the marked points is 8.5°.
Figure 17. This figure shows a zoomed image (27.4 × 27.4 nm) leveled to the facet steps of the terminal facet from Figure 13. Two hexagonal periodicities are overlaid. The first is a Si(111)-like (4 × 4), with a = 1.536 nm. The second is Si(111)-like with a = 0.384 nm. The profile (green line) is perpendicular to the step edges. The crystallographic orientation of the image’s surface is undetermined.
Figure 18. This is the profile of terminal facet in Figure 17. The average slope between the points is $2^\circ$. The step height is 0.17 nm.
orientation of the images surface is undetermined. **Figure 18** is the profile of the terminal facet in **Figure 17**. The average slope between the points marked on the image is $2^\circ$. The step heights are 0.17 nm. The terminal facet or steps form approximately $8^\circ$ angles when the [11-1] direction is rotated about [1-10] or the [1-10] is rotated about [11-1] direction. There are repeating structures formed in the terminal facet. The 0.17 nm steps could match the 1.9 nm layers of the Si(110) planes; however the angles do not match. The terminal facet region needs further study for a clearer understanding of its relationship to the bulk single crystal silicon structure.

**Figure 19**, a lower resolution image, allows mapping of the previously described structures in **Figures (10, 12-14)** to an image of the clean annealed Si(112) surface. This permits inspection of the relaxed structures in relation to each other. In this image all of the previously discussed structures are present and evidently they are independently produced by the surface variations along the [1-10] directions with the exception of features $d$ and $e$ which are connected on the surface in the [1-10] direction. **Figure 19**, feature $a$ is observed in **Figure 9** feature 1. It shows the genesis of Baski’s sawtooth-like nanofacets shown in **Figure 9**, feature 2, and mapped in this image as **Figure 19**, feature $b$. **Figure 19**, feature $c$, is similar to and maps the 2.0 nm dislocation previously explained in **Figure 12**’s description. **Figure 19**, features $d$ and $e$, are not independent of each other and indeed seem to be a complicated product of the relaxation of the Si(112) surface. They are terminal facets that average the lattice matched [1-10] direction to the Si(112)$_{cp}$ surface [1-10] direction.
Figure 19. A STM image of a Si(112) surface after four separate flash anneals to 1160°C. The image is of a lower resolution image but observes a greater surface area which helps to map the physical relationships of the higher resolution but smaller surface area images discussed earlier in this chapter. Feature a) is a non-faceted Si(112) surface, Figure 9, feature 1. Feature b) is observed in Figure 11, feature 2. Feature c) is observed in Figure 13. Feature d) is observed in Figure 9, feature (a-d)) and feature e) is observed in Figure 13, the row terminating facet.
3.3 **Continued Annealing: Six Separate Anneals of the Si(112)\textsubscript{cp} surface**

**Figure 20** is the Si(112)\textsubscript{cp} surface after 6 anneals to 1160° C. The image shows a set of 3 faceted groups of surface rows approximately 130 ±10 nm long of various widths running parallel to the [1-10] direction from beginning to end. For this image, the surface has been plane leveled to Si(112)\textsubscript{cp} plane (grey rows). The triangular dark grey regions are below the original Si(112)\textsubscript{cp} surface, and the light grey to white regions are above the original Si(112)\textsubscript{cp} surface. In this image one observes a larger area than in the previous images. All of the previous facets from **Figure 9** and the terminal facet, the region of steps between the vacancy-row and deposition regions in the [1-10] direction are included. The termination of each row has an irregular facet sloping 10° from the [112] direction in the [11-1] direction and 8° from the [112] direction in the [1-10] direction. These terminal facets have been described in detail in the earlier discussion of **Figure 13**. **Figure 21** illustrates the consistency in the faceting across a larger area of the surface and the surface structure for faceting of this degree, while maintaining the average Si(112)\textsubscript{cp} surface plane.

For the sawtooth nanofacets, described by Baski, above and below the Si(112)\textsubscript{cp} plane, a large amount of mass transport of silicon atoms from one end of the structure to the other has occurred. The volume of the vacated atoms from below the Si(112) surface to form the vacancy-row trough can be estimated as equivalent to the volume of the atoms deposited on the ridge region. These two regions are connected by single Si(111)-like facets in the [1-10] direction.

**Figure 21**, feature 1, outlines one area of faceting on the surface after 6 anneals to 1160° C. The faceting and restructuring is more developed as the ratio of the area of the original cut and polished surface to the restructured area is reduced in comparison to the less annealed images. In this image the color green represents the level of the cut and polished Si(112)\textsubscript{cp} plane.
Figure 20. A 3D perspective from a STM image (166 × 166 nm) of clean Si(112) after six separate flash anneals to 1160° C. The bias =1.8 and set point = 0.05 nA. The Z amplitude equals 2.8 nm.
Figure 21. A 3D perspective from a STM image (135 × 135 nm) of clean Si(112) after six separate flash anneals to 1160°C. The bias =1.8 and set point = 0.05 nA. The Z amplitude equals 3.1 nm. The black rectangle inscribes feature 1. Feature a) is a vacancy-row region and feature b) is a deposition region where the region are connect by Si(111)-like nanofacets.
The silicon atoms lying below the surface are indicated by feature \textit{a}) with the colors yellow, orange, red, and black. The silicon atoms arranged above the surface are indicated by feature \textit{b}) with the colors light blue, blue, violet and white. The volume of silicon atoms deposited above the surface approximately equals the volume of the silicon atoms that has been removed from the surface to expose the surface below the (112) plane. The size and shape of the mined and deposited regions are also similar.

One may describe the mass transport of the silicon atoms as follows: The silicon atoms are removed from the vacancy-row areas, moving in [-110] direction of the ridge row of the Si(111)-(7×7)-like facet plane and are deposited above the plane at the next terminal end. The length and width of these features are dependent upon the distance between the terminations of the rows.

It is also possible that mass transport is occurring in the [1-10] direction moving from the trough area to the ridge peak by traveling across the terminal facet. Generally, speculation on dynamic processes from static images is not justified. However, the observation from these images that some atoms have been vacated from and others deposited on the Si(112) surface plane, gives support to this description. It can be argued that the second process is less likely to occur because the movement of atoms across the terminal facet in the [11-1] direction, across the step edge with its significant irregularities, is a much higher energy process than that of the aforementioned process.\cite{37} In any case, it is unlikely that mass transport is occurring at the same rate in both orthogonal directions. The mode of transport is unclear from this data set. The atoms may be stepping from surface vacancy to surface vacancy, or, alternatively, traveling singly from the depression to the ridge across the surface until finding a surface vacancy to fill. These results demonstrate increased faceting with repeated annealing of the Si(112)$_{cp}$ surface.
The stages move from the assumed bulk-terminated surface (not observed in these experiments) to the nanofaceting Baski reported, to ridges and valleys formed as larger and larger areas of facets of (111) and higher index planes, as well as other terminal nanofacets are produced with repeated anneals. Finally, the surface will stabilize some evidence of the original Si(112)$_{cp}$. However, much has been replaced by the restructured surface with bulk lattice matched facets ridges and valleys in the [1-10] directions and terminal facets with the Si(112)$_{cp}$ surface average [1-10] direction of more stable but non-simplistic structures. The Si(111)-like planes of the ridges and troughs have various repeating units such as (7×7) or (5×5), depending on their width, in the [1-10] direction, although the surface is not precisely periodic on the nano-scale in the [11-1] direction.

In these experiments for the surfaces with the least annealing, the nanofacets described by Baski (2) can be identified. However, they do not comprise the larger portions of the total imaged area. The ridges and troughs produced during annealing of the Si(112)$_{cp}$ surface are caused by the reduction in the average surface energy through restructuring of the surface. The Si(112)$_{cp}$ surface plane in these experiments is off the true Si(112) by 2° in the [1-10] direction. The average surface energy is reduced by the process of atoms moving from below the Si(112)$_{cp}$ surface in the [1-10] direction and depositing them above the Si(112)$_{cp}$ surface plane forming the Si(111) nanofacets, and terminal facets that are lattice matched with the bulk (112) plane. With a Si(112)$_{cp}$ surface, cut and polished within a tolerance of 2° from the bulk (112) plane in the [1-10] direction, lattice matching while maintaining an average of the 2° off the [1-10] can be accomplished by terminating lattice matched Baski nanofacets beginning below the Si(112)$_{cp}$ surface and ending above the Si(112)$_{cp}$ surface, producing an overall average [1-10] direction.
matching the bulk crystal’s [1-10] direction. Terminal facets then return the bulk matched surface [1-10] direction to the average Si(112)cp surface [1-10] direction.

In the work I have chosen to use hexagonal periodicities overlaid on the STM images for better identification of the periodicities present in the surface as observed in the STM experiments. For all hexagonal periodicity overlays on the STM images one basis vector is oriented parallel to the [1-10] direction. The distance between the lines parallel to the [1-10] direction, or their separation in the [11-1] direction, is a projection of the across the (111) plane of the hexagonal periodicity overlay at 30°. The hexagonal periodicity used for these overlays is shown in **Figure 22**.

If A and B are two vectors in the Si(112) plane, the projection of A on B is the vector C with the same direction as B and with the length: |C| = |A| Cos(θ). The three sets of parallel lines in a hexagonal periodicity, placed parallel to the [1-10] direction and ± 30° from the [11-1] direction. The distance between the parallel lines in the [11-1] direction is (a) times the Cos(30) or (a) times 0.86603. This projection at 30° of the distances in the [11-1] direction on to the hexagonal periodicities overlaid on the STM images is applied throughout this work.
Figure 22. Hexagonal periodicity is demonstrated in this figure. The yellow lines are added to represent the placement on the images parallel to the [1-10] direction. The projection at 30° of a onto the (112) is b and equals aCos(30) or a times 0.866025 = b. The b vector is in the [11-1] direction for these placements. For example, the 9.4 nm vector in the [11-1] direction of the Si(112) bulk terminated unit cell can be represented in a hexagonal periodicity with a= 1.085 nm.
There are only three (a and integer multiples of a, hexagonal periodicity constants applied to the STM images. From the bulk-terminated unit cell two are chosen, where \( a = 0.384 \) nm in the [1-10] direction and \( b = 0.940 \) in the [11-1] direction which when projected onto the (111) plane of the hexagonal periodicity at 30\(^\circ\) gives \( a' = 1.085 \) nm. The last basic hexagonal periodicity with \( a' = 0.3905 \) nm comes from inspection of the images, their analysis and X-ray scattering results from the literature (Mochrie et al.).\(^4\) The three hexagonal periodicities with \( a = 0.384, a' = 0.3905 \) and \( a'' = 1.085 \) nm or unit factors \{(2\times2), (3\times3), (4\times4)\ldots\}, of these base periodicities, are the only hexagonal periodicities overlaid on the STM images in this study. The unit factors are used to help deal with the broad dynamic range need to cover the STM images with larger areas, greater than 20 \times 20 \) nm. For the unit hexagonal periodicities with \( a = 0.384 \) or \( a' = 0.3905 \) nm, a Si(111)-like hexagonal periodicity is employed. Unit factors of the three basic hexagonal periodicity constants in nm are show in Table 2. In Table 2 each set of colored distances indicate coincidence of the values to within less than 0.01 nm. The distances that are coincident for any two of the basic hexagonal periodicities are observed for the step structures, running parallel to the [1-10] direction, in the [11-1] direction in the STM images. The FFT power spectrum of the images in this work also identify these common distances that are consistent with these three basic hexagonal periodicities.

With regards to overlaid multiple hexagonal periodicities with differing periodicity constants and zero rotation from each other, they can be considered to be a moiré pattern. Moiré patterns as observed by STM are well presented by Kobayashi.\(^38\) Subsurface nanoscale structures can be observed with STM even if buried beneath the surface due to three-dimensional tunneling. It is possible some of the structures observed in the STM images in this work are not
generated from the local density of states from the surface layer but a convolution of the surface and the effects caused by a moiré pattern.

In an X-ray Scattering study of the clean Si(112) surface, Mochrie et al.(4) reported observing different periodicities in the [11-1] direction for five temperature regimes. Projecting these values onto the (111) plane of the hexagonal periodicity at 30°, with in the error given for each, returns values found in Table 2 for the different unit factors. Specifically, the value of 67.0 ± 1.5 nm is found for the temperature range of 857 to 882° C. This value when projected onto the (111) plane of the hexagonal periodicity at 30° is 78.1 nm. There is also a 6.7 ± 0.6 nm periodicity in this temperature range, which returns a value of 7.8 nm after projection onto the (112) plane. At the lower temperature ranges shorter periodicities were found. Using these results and the calculated values for the three hexagonal periodicities allows for better observation of the periodicities that are present in the STM images.
<table>
<thead>
<tr>
<th>Integer Multiples</th>
<th>a = 0.384 nm</th>
<th>a’ = 0.3905</th>
<th>a” = 1.085</th>
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<td>78.1 nm</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Unit factors of the three basis hexagonal periodicity constants in nm are show in this table. The color of the values for the distances, indicate coincidence of the values to within less than 0.01 nm. For example, 59 integer multiples of a’ = 0.3905 nm (a₅₉) equals 60 integer multiples of a = 0.384 nm (a₆₀) or 23.04 nm is labeled in the table in red.
Figure 23 is a color contoured STM image of the STM image in Figure 20. It has been planed to the Si(112)_{cp} surface and a hexagonal periodicity with a’_{x20} = 7.81 nm was overlaid. The Z amplitude is 2.8 nm. The hexagonal periodicity with a’_{x20} = 7.81 nm shows that the bases of the termination facets are projected at 30^0 from [11-1] direction on the Si(112)_{cp} surface. Also, the distance between the terminal facets in the [1-10] direction for this image is divisible by 7.81 nm.

Figure 24 is the STM image from Figure 9, shown with a dual hexagonal periodicity with a”_{x2} = 2.172 nm and a’_{x4} = 1.562 nm overlaid. These two lattice constants are shown here because of the quasi-periodic nature of the nanofacet in the [11-1] direction as described by Baski.(2) In this figure, the corrugations in the [11-1] direction of the rows and nanofacets running parallel to the [1-10] direction match the coincidences of the dual hexagonal periodicities in the [11-1] direction. 2.172 nm is the distance in the [11-1] direction of the \times 2 bulk-terminated Si(112) unit cell, 1.88 nm when projected onto the (111) plane of the hexagonal periodicity at 30^0. The second hexagonal periodicity is a’_{x4} = 1.562 or four units of a’ = 0.3905 nm (4\times 4). From Baski, (5) 1.57 nm units in the [11-1] is suggested. The hexagonal periodicity with a’ = 0.3905 nm is discussed in detail later in this chapter. The results of the overlaid periodicity show an intriguing insight into how these quasi-periodic rows may have long range order controlling their restructuring in the clean annealed Si(112) surface.
Figure 23. This is a 2D perspective from the STM image in Figure 20 with a Si(111)-like hexagonal periodicity with a = 7.81 nm (a"×20 = 0.3905 nm (20×20)) overlaid.
Figure 24. The STM image from Figure 9 is shown with a dual hexagonal periodicity with $a''_{x2} = 2.172$ nm ($a'' = 1.085$ nm ($2 \times 2$)) and $a'_{x4} = 1.562$ nm ($a' = 0.3905$ nm ($4 \times 4$)) overlaid.
3.4 **Negative bias for STM imaging of the annealed Si(112)$_{cp}$ surface**

The following section relates to STM images of a Si(112)$_{cp}$ surface annealed to 1200° C. The STM images were obtained with a bias of -1.8 Volts and a set point of 0.05 nm on two adjacent regions in the [1-10] direction, on the sample surface. **Figure 25** is a STM image (46.3 × 46.3 nm) of a deposition region of the sample surface where Si atoms have restructured, been transported and then deposited on top of the original Si(112)$_{cp}$ surface. **Figure 30** is a STM image (40.0 nm × 40.0 nm) of a vacancy-row region with a step or terminal facet, in the [1-10] direction.

In the region shown in **Figure 25**, the silicon atoms of this surface have been deposited onto the Si(112)$_{cp}$ surface. Both Si(111)-like and Si(113)-like facets running parallel to the [1-10] direction identified by their angles to the (112) plane rotated about the [1-10], 20 ± 1° and 10.5 ± 1° are observed in this image. A third facet 2.0 nm wide in the [11-1] direction with repeating 2.0 nm structures running in the [1-10] direction is also observed. This ridge row occurs where the (111) and (113) facets meet in the [11-1] direction parallel to the [1-10] above the (112) plane.

**Figure 26,** is a color contoured zoom (8.0 × 8.0 nm) of (**Figure 25,** Feature A) which depicts a Si(111)-like hexagonal periodicity with \( a = 0.384 \) nm overlaid on the image. For the local area in this image the hexagonal periodicity with \( a = 0.384 \) nm matches well with a corrugation height in this direction of \( 0.17 ± 0.01 \) nm for the features (lighter gray) running along the top row in the [1-10] direction. This corrugation height is less than a single Si(111) layer in thickness. In this instance, the lattice is useful as an accurate representation of atomic spacing in the [1-10] direction for the image. After global leveling to the (112) plane, the distortion in the [11-1] direction for the Si(111)-like hexagonal periodicity is scaled by -6%. The sharpness,
Figure 25. A (46.3 × 46.3nm) STM image of the Si(112) surface after eight separate flash anneals to 1160° C. The set point is 0.05 nA and the bias is -1.8 Volts. The Z amplitude is 1.65 nm. Repeating structures along the [1-10] direction are observed. In Feature A, the angle of the slope is 19.5 ± 0.7° in the [-1-11] direction and 10.0 ± 1.0° in the [11-1].
Figure 26. Feature A is a 8.0 × 8.0 nm zoom from Figure 25 with a Si(111)-like hexagonal periodicity with a = 0.384 nm overlaid. The set point is 0.05 nA and bias is -1.8 V. The Z amplitude is 1.6 nm. The corrugation height in the Z direction is 0.17 ± 0.01 nm. The slope in the [11-1] direction for the lower half of this image, below the ridge row, is 19.2° and 10° above the ridge row.
corrugation, and periodicity of the ridge structure are difficult to explain completely by conventional lattice matching. When the Si(111)-like and Si(113)-like planes meet at the surface a ridge row is formed. The ridge row is 2.0 nm wide in the [11-1] direction with 2.0 × 2.0 nm structures repeating in the [1-10] direction. In Figure 25, when viewing longer distances in the [1-10] direction on the ridge row, it is apparent there are 0.384 nm dislocations every two, three, or four (2.0 × 2.0 nm) units. For small neighborhoods, this Si(111)-like hexagonal periodicity with a = 0.384 nm matches well in the [1-10] direction but over longer distances, it does not predict the surface periodicity.

Figure 27, panel a), is a structural model of the cross section of the ridge rows. The blue line indicates the plane of the 2.0 nm wide ridge rows. The blue vector is normal to the ridge row plane and is rotated about the [1-10] direction, in the [11-1] direction, 2° off the [112] direction. Panel b) is a 3D perspective of Figure 25. The green arrows show the approximate placement of the cross section from panel a) into the 3D image in panel b).
Figure 27. Panel a) is a structural model of the cross section of the ridge rows. The blue line indicates the plane of the 2.0 nm wide ridge rows. The blue vector is normal to the ridge row plane. The blue vector is rotated about the [1-10], in the [11-1] direction, 2° off the [112] direction. Panel b) is a 3D perspective of Figure 25. The green arrows show the approximate placement of the cross section from panel a) into the 3D image in panel b).
**Figures (28-29)** compare longer distances in the [1-10] direction on 4 separate ridge rows. **Figure 28, 1)** is a 55 \times 30 \text{ nm} zoom of **Figure 25** with four profiles locations mapped, \(a\) to \(d\). These profiles run in the [1-10] direction across the top of the ridge row. In plot 2) (\(a-d\)), the Z amplitude vs. the profiles of the [1-10] direction, are compared to each other. The Z amplitudes are consistent within each profile but there is variation in the average height from 0.8 to 1.7 nm for the four profiles. **In Figure 29, plot 1)**, the four profiles were translated in the [1-10] direction so that all peak-to-peak distances matched. The shapes and relative amplitudes of the matched peaks for all four profiles match. **In Figure 29, plot 2)**, the FFT of each profile is shown. The major peak in each of the profile FFTs show a 2.05 nm periodicity. The profiles of the corrugation in each ridge row are identical in peak-to-peak distances, however, those individual distances are not precisely 2.05 nm. Within the dimensions of this image, no periodic distance greater than the average 2.05 nm periodicity in the [1-10] direction is observed. A longer range ordering process is indicated.
Figure 28. Image 1) is a $55 \times 30$ nm zoom of Figure 25 with 4 profiles locations mapped, a) to d). In plot 2) (a-d), the profiles, $Z$-amplitudes vs. distance along the [1-10] direction are compared.
Figure 29. When the profiles from Figure 28 plot 2) are translated in the [1-10] direction to match the peak-to-peak distances, all of the peak-to-peak distances for 1) a-d match. Plot 2) (a-d) is the FFT of each profile from Figure 28, plot 2) (a-d). The FFT of each profile shows a peak periodicity at 2.05 nm. Within the dimensions of this image, no periodic distance larger than the average 2.05 nm in the [1-10] direction is observed. Long range ordering of greater than 60 nm is indicated.
**Figure 30** is a $40.0 \times 40.0$ nm STM image of the same surface as in **Figure 25**. The bias equals 1.8 V and the set point equals 0.05 nA. It is of the same region on the surface and a 2 nm portion of the left side of the image is the same area as imaged on the right 2 nm portion of **Figure 25**. A step between the vacancy-row region in the [-110] direction (to the left in the image) of the white line and the deposition region in the [1-10] direction (to the right in the image) of the white line is observed. The bottom of the image is in the Si(112) surface plane and the Z amplitude is 1.28 nm. This is a slightly higher resolution image and greater detail in the surface structures can be observed.

**Figure 31** is a 3D perspective from zoomed portion ($35.8 \times 35.8$ nm) of the STM image from **Figure 30**. The original image was rotated to be horizontal to the [1-10] direction and subsequently planed to (113) facets. The Z amplitude = 3.8 nm with the top of the image the highest region. Rows run in the [1-10] direction, with repeating structures on the ridge rows as described for **Figure 25**. In addition there is more detail in this image showing that these structures are very close to identical but do vary slightly in the [1-10] direction. The FFT of a profile of these ridges in the [1-10] direction produces a strong peak at a periodicity equal to 2.06 nm. The widths in the [11-1] direction of the (113) facet running in the [1-10] direction are varied. Features a) and b) are in the Si(112) plane with visibly less reconstruction. Line a) runs parallel to the [1-10] direction and the FFT of this profile shows a strong peak for the periodicity of 0.38 nm. This would be expected on the bulk-terminated Si(112) surface. Line b) is parallel to the fine lines in the image running $6^\circ$ off the [11-1] direction rotated about the [112] direction toward the [1-10] direction.
Figure 30. A 40.0 × 40.0 nm STM image of a Si(112) surface after eight separate flash anneals to 1160° C. The bias = -1.8 V and set point = 0.05 nA. The Z amplitude is 1.28 nm. A step between the vacancy-row region in the [-110] direction of the white line and the deposition region in the [1-10] direction of the white line is observed.
Figure 31. This is a 3D perspective from a zoomed portion (35.8 × 35.8 nm) of the STM image from Figure 30. The original image was rotated to be horizontal to the [1-10] direction and subsequently planed to (113) facets. The Z amplitude = 3.8 nm, with the top of the image the highest region. Line a) marks a profile in the [1-10] direction and line b) follows the fine line features in the image.
The similar rows, parallel to the [1-10] direction, shift 1.43 nm in the [11-1] direction, when translating from feature a) (vacancy-row region), to feature b,) which is a deposition region. Due to the size of the area of the STM images and the long range ordering in the [1-10] direction, the shift for translation in the [1-10] direction is not determined. The step height is 0.54 nm in the [11-2] direction between similar features on the rows in box a) and b) where feature b) is higher. The lattice constant for the bulk single crystal silicon is 0.543 nm. The structures are matched after translation indicating long range ordering in both the [1-10] and [11-1] direction. The distance in the [11-1] direction for both the a) vacancy-row region and b) deposition region is 19.95 nm. The distance 19.95 nm projected across the (112) plane at 30° from the [11-1] direction is 23.04 nm. 23.04 nm is 60 units of a Si(111)-like hexagonal periodicity with a=0.384 nm. If there is also a second Si(111)-like hexagonal periodicity coincident at 23.04 nm, then it also should be some number of whole units and not evenly divisible into 60. The simplest solution would be 59 units of a’ = x equals 60 units of a = 0.384 nm. Solving for a’, gives a’ = 0.3905 nm. If dual Si(111)-like hexagonal periodicities are at least in part causing the long range ordering, then overlaying a Si(111)-like hexagonal periodicity with a’ = 0.3905 nm should also match the features in the STM images of this surface.
Figure 32. This a zoomed image (40 × 30 nm) of Figure 30. The step height is 0.54 nm in the [112] direction between similar features on the rows in box a) and b) where feature b) is higher. The similar rows, parallel to the [1-10] direction, shift 1.43 nm in the [11-1] direction (at c, the horizontal red double arrow), when translating from similar rows in box a) to b).
Figure 33 is a zoomed image (39.3 × 23.5 nm) of the STM image in Figure 30 with a Si(111)-like hexagonal periodicity with a’ = 0.3905 nm overlaid parallel to the [1-10] direction. The zoomed image was plane leveled to the dark red layer, feature a), across the whole image.

Feature b) is a Si(111)-like facet rotated 19.5° about the [1-10] direction, in the [-1-11] direction from the [112] direction. Making the observation that this facet is below the ideal Si(112) surface plane and that the bulk atoms in this facet may not have been removed from the bulk Si crystal, it is reasonable to assume that the plane of the image is then 2° off the ideal Si(112) plane when rotated in the [11-1] direction, about the [1-10] direction. This 2° rotation is discussed in connection with Figure 9.

The Z amplitude of Figure 33 equals 1.5 nm. The Si(111)-like hexagonal periodicity with a’ = 0.3905 nm matches the imaged peaks of the structures observed along the rows in both the [1-10] and [11-1] directions for all three areas; the vacancy-row region, the step region (terminal facet) and the deposition region. A planar Si(111)-like hexagonal periodicity with a’ = 0.3905 describes the two dimensional projection, in the [1-10] and [11-1] directions, of the topology for this image of the reconstructed clean annealed Si(112) surface when overlaid. Once again, long range ordering of the surface reconstruction is apparent.

It is a complex challenge to lattice match this surface to the bulk-terminated single crystal Si(112) plane and so far has been unsuccessful. Of the crystal planes described by Baski, the closest in angle for the rotation about the [1-10] direction is Si(337) (length in the [11-1] direction = 1.57 nm) at 4.1° from the Si(112) plane, and Si(5 5 12) has even a greater rotation of 4.8° from the Si(112) (length in the [11-1] direction = 5.35 nm). There is no silicon surface plane less than 5.35 nm in length in the [11-1] direction that is 2° off the Si(112) plane. There is
Figure 33. A zoomed image (39.3 × 23.5 nm) of the STM image in Figure 30 with a Si(111)-like hexagonal periodicity with a = 0.3905 nm overlaid parallel to the [1-10] direction. The zoomed image was plane leveled to the dark red layer, feature a), across the whole image and is 2° off the Si(112) plane when rotated in the [11-1] direction, about the [1-10] direction. The Si(111)-like hexagonal periodicity with a = 0.3905 nm matches in both the [1-10] and [11-1] directions. Feature b) is a Si(111)-like facet rotated 19.5° about the [1-10] direction, in the [-1-11] direction from the [112] direction. The Z amplitude equals 1.5 nm.
no surface plane for silicon that has a unit cell [11-1] vector of 2.0 nm. On the other hand, silicene (an allotrope of silicon with a structure similar to graphene) forms very regular rows 2.0 nm wide in the [1-11] direction running at length along the [-110] on Ag(110). (39)

There are several striking properties of silicone ribbons that are described in detail by Kara et. al.(40) They report that silicene demonstrates chirality, a Z amplitude height of 0.2 nm, has metallic character, a slightly arched cross section and asymmetry in its cross-section, and a honeycomb lattice. (39-40)

Each of these characteristic features of silicene is supported in the STM images of the clean high temperature annealed Si(112) surface in Figures (25-33). The ridge rows are 2.0 nm wide in the [11-1] direction and run long range (>60.0 nm) in the [1-10] direction.(39) The chirality is evident in Figure 33 along the Si(113) like facet side of the ridge row edges. The Z amplitude for the corrugation of the ridge rows in the [1-10] direction is 0.17 nm, which is within 15 percent of the 0.2 nm value given for the height in the Z direction of silicene. The RMS surface roughness for the Si(111)-like facets and the Si(113)-like-facets from the STM images is what might be expected from a metal surface rather than from a semiconducting surface. The ridge rows running in the [1-10] direction, are asymmetric and arched over the ridge peak where the Si(111)-like and Si(113)-like facet meet at the surface running in the [1-10] direction. There is hexagonal periodicity with a’ = 0.3905 nm across the whole surface in Figure 33.

All of these features in the STM images lend support for the existence of a silicene-like surface layer. Although this is a compelling argument, further work is required to produce a more definitive conclusion.

In this section several periodicities were identified in the STM images of the clean Si(112) surface after 8 anneals to 1160° C. The ridge row structures in the [1-10] direction have
a periodicity of 2.05 nm. They also have long range ordering, which if repeating has a periodicity larger than 60 nm. A planar Si(111)-like hexagonal periodicity with $a' = 0.3905$ nm describes the two dimensional projection, in the [1-10] and [11-1] directions, of the topology of the vacancy-row and deposition regions of this surface. This could indicate the presence of a silicene-like surface layer covering these regions.
3.5 **STM, FFT and LEED of the high temperature annealed the Si(112)$_{cp}$ surface**

3.5.1 **Introduction**

For this section a clean Si(112) sample was annealed to 1200° C for 24 hours and the resulting surface was imaged by STM (Figure 34). A series of hexagonal periodicities are matched to the STM image. The LEED pattern of a high temperature annealed Si(112) surface is analyzed and matched to a centered rectangular unit cell. The points on the FFT of this STM image and the lattice constants of dual hexagonal periodicities overlaid on the STM image are matched.

3.5.2 **STM of the high temperature annealed Si(112)$_{cp}$ surface**

Figure 34 is a 57.1 × 57.1 nm STM image of a high temperature annealed Si(112) surface. The bias = 1.8 V and set point = 0.05 nA. It has a Z-amplitude of 1.0 nm. There are observable rows in the [1-10] direction. Overlaid on the image with one of the lattice vectors parallel to the [1-10] direction is a hexagonal periodicity with $a = 7.81$ nm. As described previously in the discussion of Figure 22. This lattice constant is chosen for two reasons. First, it is exactly 20 units of the hexagonal periodicity with $a' = 0.3905$ nm found to match the images in Section 3.4 and second, it matches, within the error the X-ray scattering results described by Mochrie et al. (4) where $6.7 ± 0.6$ nm in the [11-1] direction projected in the (112) plane at 30° equals $7.74 ± 0.7$ nm. The placement of this periodicity is aligned with 4 step rows parallel to the [1-10] direction. This imaged region with an overall Z-Amplitude of 1.0 nm is planed to the average Si(112) plane. The placement of the center of the hexagonal periodicity was chosen to match the [1-10] direction of the image as well as matching the structures in the bright center row. The hexagonal periodicity with $a = 7.81$nm agrees with Mochrie’s et al. (4) observations.
described for the 1139 to 1155 K temperature regime producing a periodicity of 6.7 ± .6 nm in the [11-1] direction reconstructions on the Si(112) annealed surface.

In Figure 35 additional hexagonal periodicities with $a''_{x9} = 9.765$ and $a'_{x100} = 39.05$ nm are overlaid. The hexagonal periodicity placements are similar to Figure 34. The hexagonal periodicity lattice with $a''_{x9} = 9.765$ nm is chosen from the convergence of lattice constants. The first is based on the bulk unit cell distance in the [11-1] direction of 9.40 nm projected in the (112) plane at 30° = 1.085 nm. Nine units of 1.085 nm is equal to 9.765 nm. The second hexagonal periodicity with $a' = 0.3905$ nm is from Chapter 3.4. Twenty five units of $a'_{x25} = 0.3905$ nm equals 9.763 nm. Finally, 4 units of 9.763 and 5 units of 7.81 nm are both equal to 39.05 nm. In this image, all but two of the steps parallel to the [1-10] direction are traced by the lines produce by the dual hexagonal periodicities in the [1-10] direction. Each line in the [1-10] direction of the hexagonal periodicities follows parallel to a step feature. There is apparent long-range ordering in the [11-1] direction.

A dual hexagonal periodicity with $a'_{x5} = 1.953$ nm and $a''_{x2} = 2.17$ nm are overlaid in Figure 36. The first hexagonal periodicity produces the three previous hexagonal periodicities overlaid in Figure 35 and is five units of the hexagonal periodicity with $a = 0.3905$ nm used to match the STM images in Chapter 3.4. The second is the distance of 1.88 nm for the $\times$2 bulk-terminated Si(112) units in the [11-1] direction, when projected in the (112) plane at 30° equals 2.17 nm. These dual hexagonal periodicities overlaid on the image, shows good correlation with the rows observed in the [1-10] direction.
Figure 34. This figure is a 57.1 × 57.1 nm STM image of a clean 1200°C (high temperature) annealed Si(112) surface. The image is overlaid with a hexagonal periodicity with $a'_{x2\theta} = 7.81$ nm. The surface was imaged at a bias of 1.8 V and a set point of 0.05 nA. The $Z$ amplitude is 1.0 nm.
Figure 35. This figure shows Figure 34 with two additional hexagonal periodicities with $a'_x 25 = 9.763$ and $a'_x 100 = 39.05$ nm (red).
Figure 36. Dual hexagonal periodicities with $a''_{x2} = 2.17$ and $a'_{x5} = 1.953$ nm are overlaid on the image from Figure 34.
Further, in Figure 37 the FFT of this STM image produces lines in the [11-1] direction centered on the [1-10] axis at the points of 2.04, 1.17, 1.08, 0.781 and 0.768 nm. All of these points are unit factors of one of the three hexagonal periodicities used for this work. It is possible to reduce the lattice constants of the two periodicities further; however, at this scale it becomes difficult to observe the details. The third hexagonal periodicity which is equivalent to two units of Si(111)-(1×1) hexagonal periodicity with $a = 0.384$ nm or $a \times 2 = 0.768$ nm, is not shown for the same reason.

These first four Figures (34-37) all show the consistency of the hexagonal periodicity with periodicity matching along the rows in the [1-10] direction as well. Additionally, from Figure 36 the superposition of the two hexagonal periodicities produces a pattern that roughly follows the smoother and rougher surface regions in both the [11-1] and [1-10] directions.
Figure 37. The image of the FFT of Figure 34 is shown. The lines in the [11-1] direction are centered on the [1-10] direction at 2.04, 1.17, 1.08, 0.781 and 0.768 nm periodicities.
3.5.3 Dual Si(111)-like hexagonal periodicities overlays

The next three Figures (38-40) are of a (24.1 × 30.8 nm) zoom of the lower right area of Figure 34. In Figure 38, region A) has the greatest height of the surface corrugation, region B) has a medium height of corrugation and region C) has a low height of corrugation. In Figure 39 a Si(111)-like hexagonal periodicity with a’ = 0.3905 nm is overlaid on the zoomed image from Figure 38. The placement of the periodicity brings out the order in a seemingly disordered region. There is a long range ordering process acting on this surface resulting in Si(111)-like hexagonal periodicity with a’ = 0.3905 nm.

The last figure (Figure 40) in this series of three, is the same image as in Figure 39 but with a second Si(112)-like hexagonal periodicity with a = 0.384 nm overlaid. The resulting moiré pattern shows good correlation at the atomic level in the regions of different corrugation height. When the Z amplitudes are highest, the two Si(111)-like hexagonal periodicities are coincident. When the two Si(111)-like hexagonal periodicities are non-coincident the Z amplitudes are the lowest. Attempts to lattice match this surface to the bulk-terminated Si(112) surface in either the [1-10] or the [11-1] direction met with failure do the this dual periodicity on the surface.
Figure 38. A $24.1 \times 30.8$ nm zoom of the STM image in Figure 34. The Z amplitude is 1.0 nm. Region A) is an area of high surface corrugation, region B) is an area of medium corrugation and region C) is an area of low surface corrugation in the Z direction.
Figure 39. The STM image in Figure 38 with an overlay of a Si(111)-like hexagonal periodicity with a=0.3905 nm.
Figure 40. The STM image in Figure 38 with an overlay of dual Si(111)-like hexagonal periodicities with $a = 0.384 \text{ nm}$ and $a' = 0.3905$. 
The next set of four figures (41-44) are of a 14.4 × 14.4 nm zoom of the region A in Figure 38. The increased resolution has not brought out any obvious long range ordering. Once again as shown in Figure 44, careful placement of the dual hexagonal periodicities with a’ = 0.3905 nm from Figure 42 and a = 0.384 nm from Figure 43 when combined shows a strong correlation to the image’s features.

The moiré pattern once again is observed to correlate well with the height of corrugation. If the surface atoms are centered on a hexagonal periodicity with a’ = 0.3905 nm and the second layer of atoms are centered on a hexagonal periodicity with a = 0.384, then the resulting density of states observed in the STM experiment might well be an interference pattern similar to what is observed.
Figure 41. This figure shows a 14.4 × 14.4 nm zoomed image of Figure 38, region A). The surface was imaged at a bias of 2.0 V and a set point of 0.05 nA. The Z amplitude is 0.77 nm.
Figure 42. A Si(111)-like hexagonal periodicity with $a' = 0.3905$ nm is overlaid on the image from Figure 41 for this figure.
Figure 43. A Si(111)-like hexagonal periodicity with $a = 0.384 \text{ nm}$ is overlaid on the image from Figure 41 for this figure.
Figure 44. Dual Si(111)-like hexagonal periodicities with $a = 0.384$ nm and $a' = 0.3905$ nm are overlaid on the image from Figure 41 for this figure.
3.5.4 FFT analysis of clean high temperature annealed Si(112)

The next set of figures (45-47) show the results of a FFT analysis of the zoomed region in Figure 41. Figure 45 is the original FFT of the image. Figure 46 is the pass filtered points chosen from the complete FFT. Figure 47 is the inverse FFT of the pass filtered points with two Si(111)-like hexagonal periodicities, \( a = 0.384 \) nm, \( a' = 0.3905 \) nm and hexagonal periodicity \( a'' = 1.085 \) nm overlays. The third hexagonal periodicity \( a' = 1.085 \) nm was added in an attempt to better visualize the underlying Si(112) bulk-terminated unit cell in the [11-1] direction. The distance between the lines parallel to the [1-10] direction, in the [11-1] direction is 0.94 nm. Once again there is strong correlation between the image and the hexagonal periodicity interference patterns. Also of note is the thickness of this FFT pass filter generated image. Its Z amplitude is 0.17 nm, which is the height of corrugation found for the ridge rows in the [1-10] direction in other clean annealed Si(112) surfaces shown in Chapter 3.4.

At the center of the image, the expected structure, a Si(112) unit cell can be observed with edge, terrace, and trench atoms arranged reasonably. However, there is a 10° rotation for the corrugation height about the [112] direction, which cannot be accounted for if these atoms are lattice matched to the bulk terminated Si(112) surface.

It can be concluded that there is a long range ordering process that is a convolution of three planar layered hexagonal periodicities with \( a = 0.384 \) nm, \( a' = 0.3905 \) nm, and \( a'' = 1.085 \). The first two account for local surface structures and the third, based on the Si(112) unit cell, accounts for the long range order in the [11-1] direction.
Figure 45. This figure is an image of the FFT of the STM image in Figure 41. The square root of the Z amplitude is displayed.
Figure 46. The pass filter FFT points of the full FFT in Figure 45 are shown. The distances labeling the points are in nm.
Figure 47. The inverse FFT of the pass filter FFT points only from Figure 46. The Z amplitude is 0.17 nm. Two Si(111)-like hexagonal periodicities, with $a = 0.384$ nm and $a' = 0.3905$ nm and along with a hexagonal periodicity with $a'' = 1.085$ nm, are overlaid in this image.
3.5.5 **LEED of clean high temperature annealed Si(112)**

*Figure 48* is a LEED image of clean annealed Si(112) taken at a beam energy of 140 eV with a proposed hexagonal unit cell with $a = 0.623$ nm shown by the yellow lines. The distance of 0.623 nm is 2/3 of the Si(112) unit in the [11-1] direction. Using the analysis software program, LEED pattern simulator (LEEDpat Version 3.0) developed by K. Hermann and M. A. Van Hove, a reduced fitting of the above hand fitted pattern suggested by the program can be accomplished with a centered rectangular unit cell with $a = 0.384$ nm and $b = 3.516$ nm. In *Figure 49*, LEED peaks in rows 1 and 2 are matched in the [11-1] direction on a centered rectangle $a = 0.384$ nm $b = 3.516$. In rows 3, 4 and 5 the reciprocal lattice points are located between the LEED peaks in the [11-1] direction. In *Figure 50*, a similar fitting can be accomplished with this centered rectangular unit cell when rows 3, 4 and 5 are matched to the LEED peaks and rows 1 and 2 are located between the peaks. For both *Figures (49,50)*, all the rows align in the [1-10] direction.
Figure 48. This is a LEED image of clean annealed Si(112) with a proposed hexagonal unit cell with $a = 0.623$ nm. The rectangular unit cell would be 0.768 nm in the [1-10] direction and 0.623 nm in the [11-1] direction. 0.623 nm is 2/3 of the Si(112) lattice constant in the [11-1] direction. The LEED image was taken at 140 eV.
Figure 49. The first and second vertical rows are centered in the [11-1] direction on a centered rectangle with $a = 0.384 \text{ nm}$, $b = 3.516 \text{ nm}$. All the rows align in the [1-10] direction. LEED image taken at 140 eV of clean high temperature annealed Si(211).
Figure 50. The third, fourth and fifth vertical rows are centered in the [11-1] direction on a centered rectangle with \(a = 0.384\) nm, \(b = 3.516\) nm. All the rows align in the [1-10] direction. LEED image taken at 140 eV of clean high temperature annealed Si(211).
Figure 51 shows the a) real and b) reciprocal lattices for a centered rectangle (blue rectangle) with $a = 0.384$ nm and $b = 3.516$ nm. Doubling the $b$ constant to 7.032 nm does not improve the fitting of the software generated inverse lattice points to the observed pattern. A primitive oblique unit cell (lower symmetry) with $a_s = b_s = 1.77$ nm (red vectors) and $\phi_s = 167.9^\circ$ is shown in panel a). Figure 51 feature c) is a zoom $(30 \times 15$ nm) of Figure 31 with the algorithm generated real lattice overlaid. The Z amplitude is equal to 0.88 nm. The image of the generated real lattice was fitted to the 0.384 nm lattice points parallel to the [1-10] direction. The angle of the real lattice is observed to be the same for the fine lines in this image at a periodicity of 0.384 nm in the [1-10] direction. This supports the conclusion that the features observed in this region of the STM of clean high temperature annealed Si(112), are what produced the LEED pattern we observed for this surface.
Figure 51. The a) real and b) reciprocal lattices for a centered rectangle are shown. The blue rectangle in a) defines the centered rectangle unit cell with $a = 0.384$ nm, $b = 3.516$ nm and $\phi = 90^\circ$. The green outline shows the primitive oblique unit cell (lower symmetry) with $a_s = b_s = 1.77$ nm (red vectors) and $\phi_{s} = 167.9^\circ$. Feature c) is a zoom ($30 \times 15$ nm) of Figure 31 with the algorithm-generated real lattice overlaid. The Z amplitude is equal to 0.88 nm. The black vectors (arrows) are the a and b lattice constants (both = 1.77 nm and $\phi_{s} = 167.9^\circ$) for the primitive oblique unit cell.
3.6 Conclusions

In this chapter a survey of STM and LEED images of clean annealed Si(112) surfaces were analyzed and compared. In section 3.3 short multiple anneals of the Si(112) surface that produced nanofaceting as well as new features were described. The nanofaceting has been described previously by Baski.(2)

There is a slope 2° off the [112] direction about the [11-1] running on the ridge tops of Si(111)-like nanofacets in the [1-10] direction. The nanofacet starts above the Si(112)$_{cp}$ at the edge of the terminal facet and runs in the [1-10] direction below the Si(112)$_{cp}$ surface to the bottom of the next terminal facet. Vacancy-row regions run in the [1-10] direction below the surface and are widest, in the [11-1] direction, next to the terminal facet. As the depth of the depression increases, the width of the depression also increases creating a triangular depression in the surface. The deposition regions are widest, in the [11-1] direction and have the greatest Z amplitude at the edge of the terminal facet, creating a triangular peak above the Si(112)$_{cp}$ plane. By inspection of these two structures in the images, the volume of atoms removed from the vacancy-row region seems to equal the volume of atoms deposited in the deposition region. The two regions are connected to each other by a Si(111)-like nanofacet in the [-110] direction. The greater the distance between the vacancy-row region and the deposition region in the [1-10] direction, the larger the volumes in those regions. The deposition region is not commensurate with the Si(112) surface.

In section 3.4, a long range periodicity of 2.04 in the [1-10] direction was identified along the ridge rows of the nanofacets where the Si(111)-like facets meet at the surface of the Si(113)-like facets in the [11-1] direction. A Si(111)-like hexagonal periodicity with a’ = 0.3905 nm fits the surface structures well when overlaid on both the vacancy-row and deposition regions.
An STM image of a clean high temperature annealed, 1200° C, Si(112) surface revealed periodicity in the [11-1] direction. An overlaid dual hexagonal periodicity with a”x2 = 2.17 nm and a”x5 = 1.953 nm fits well in the [11-1] direction. The average periodicity for these two periodicities in the [11-1] direction is 1.78 nm. LEED pattern matching for this surface shows a centered rectangle with a = 0.384 nm, and b = 3.516 nm. In a 14 × 14 nm zoom of this surface, a dual Si(111)-like hexagonal periodicity with a = 0.384 nm and a’ = 0.3905 nm shows strong agreement with the STM image.
4. ARSENIC DEPOSITION ON CLEAN ANNEALED SILICON (112)

4.1 Introduction

This chapter addresses the arsenic precursor layer deposited during the annealing step in which the MBE growth process is used for producing high quality single crystal Si(112)/As/ZnTe/CdTe thin films. This research has significant implications for basic surface science, as well as economic and environmental potential aspects for thin film technology. From the surface structure point of reference, a better understanding of the role arsenic plays in forming the best substrate discovered to date for high quality single crystal CdTe thin film growth will be useful for advancements in surface science technology.

Cadmium telluride, an inorganic single crystal, is an intrinsic semiconductor with a zinc blende crystalline structure. It has a band gap of 1.44 eV along with high absorption which is an excellent match for the energy of the photons in the solar spectrum. Although CdTe is most often used in PV devices without being alloyed, it is easily alloyed with zinc, mercury, and a few other elements to vary its properties. Thin films of CdTe can be manufactured using low-cost techniques, including closed-space sublimation, electrochemical deposition, and chemical vapor deposition. The highest quality CdTe thin films are produced by MBE growth process on Si(112) substrates. These CdTe thin films cost the most to produce. However, studying and understanding the processes involved and their use in producing these films will give better insight into what is necessary for high quality CdTe single crystal thin film growth. In turn, these insights might lead to the development of lower cost processes for producing CdTe thin films for photovoltaics.
4.2 Motivation

The combination of three surface science analytical techniques, XPS, LEED, and STM, was used to study the MBE deposition of a monolayer of arsenic on the clean Si(112) surface to provided greater insight as to the structure of the As monolayer on Si (112) and its role in MBE growth of thin film CdTe on Si(112). As described earlier in this work, a better understanding of the physical structure and rearrangements of arsenic adatoms on Si(112) may lead to improved MBE growth processes and therefore improved the quality of CdTe thin films grown by MBE.

4.3 Arsenic deposition procedure

Arsenic is deposited as a precursor layer during the initial annealing step of the Si(112) surface during MBE growth of CdTe thin films. In 1994, it was found that this As monolayer significantly improves the quality of thin films of CdTe on Si(112). In the literature, it has been hypothesized that the monolayer of arsenic may possibly function as a passivant and/or surfactant on the surface of Si(112) substrate during the MBE growth of CdTe thin films. As a passivant, its role would be to protect the clean Si(112) surface from impurities located on the surface. As a surfactant would be to prevent the Te adatoms from bonding to sites that would cause defects in the single crystal growth, allowing them to move across the surface until they bond to suitable sites for epitaxial growth.

This chapter presents an alternative hypothesis strongly supported by data that arsenic forms, with fast kinetics, a low energy surface preventing rearrangement of silicon atoms on the surface. This surface is better suited for epitaxial growth of thin film CdTe on Si(112) than the Si(112) surface annealed without the arsenic precursor monolayer. In this study, STM, LEED
and XPS analysis of MBE deposited arsenic monolayers on clean annealed Si(112) are presented.

The arsenic deposition chamber designed and built for these experiments is described in Chapter 2. For these experiments, Si(112) substrate samples were prepared by the modified RCA treatment step described in Appendix I followed by a single annealing step, and then deposition of a monolayer of arsenic on the clean silicon in the preparation chamber. For the silicon surfaces studied in these experiments, the monolayer As deposition procedures were modeled upon the MBE recipe employed by MPL for CdTe thin film growth on Si(112). This involved one annealing cycle with As$_4$ deposited during the cooling phase. The flash anneal while heated up to 1150°C at 2°C/second was without As$_4$ flux. Then, under an As$_4$ molecular beam, with the preparation chamber pressure increased to $1 \times 10^{-8}$ Torr from the As$_4$ source, the sample was held at 1150°C for 20 seconds as the temperature was ramped down from 1050°C to 380°C. After allowing the sample to cool to ambient temperature, the sample was transferred from the preparation chamber to the analysis chamber in situ for LEED, XPS, and STM analysis.

4.4 **Scanning Tunneling Microscopy results for MBE grown Si(112)/As**

After deposition of the arsenic, both LEED and XPS experiments were performed on the prepared sample. The XPS results consistently demonstrated strong Si and As peaks, with C and O signals at the most just above the noise level. These experimental surfaces were Si(112)/As. It is significant that after the single annealing cycle the LEED was clear and the STM images were obtained. Normally, three to four repeated anneals are required on a clean silicon surface to create a surface suitable for quality STM imaging.
Figure 52 is a STM image of a Si(112)/As surface. This image covers an area of 61.2 × 61.2 nm with a Z amplitude of 2.24 nm. The step height for the adlayer rows is 0.30 ± 0.05 nm. The brightest spots are 0.7 nm in height leaving 1.5 nm in height for the adlayers of rows, or five to six levels for the adlayer rows in the Z direction. Figure 53 is a 3D projection that illustrates the rows and layering of the arsenic on the Si(112)/As surface. In this image the Z amplitude is 1.4 nm and four levels of the 2.0 nm wide rows running in the [11-1] direction are observable.

Figure 54 is a FFT of the STM image from Figure 52. Specific points can be identified, first in the [11-1] direction; there are 1.08 and 2.03 nm periodicities. These points can be attributed to the projection at 30° in the (112) plane of 1.17 nm (Si(111)-like periodicity with a = 0.3905 nm (3×3) ) and 2.34 nm (Si(111)-like periodicity with a = 0.3905 nm (6×6) ). In the [1-10] direction, 39.1 nm and 78.1 nm are given by the FFT point measurement routine in the WSxM analysis software, although near the limit of resolution of the digitized data. All of these periodicities can be assigned to multiple units of the hexagonal periodicity with a’ = 0.3905 nm. It is reasonable to make use of an overlaid hexagonal periodicity with a’×6 = 2.34 nm or a Si(111)-like periodicity with a’ = 0.3905 nm for this surface to help visualize the overall periodicity in the [11-1] direction.
Figure 52. A STM image of Si(112)/As, (61.2 × 61.2 nm). The surface was imaged at a bias = 2.0 V and a set point of 0.05 nA. The Z amplitude is 2.24 nm.
Figure 53. A 3D perspective of a Si(112)/As surface, (24.8 × 62 nm). The surface was imaged at a bias = 2.0 V and a set point of 0.05 nA. The Z amplitude is 1.4 nm.
Figure 54. A FFT image of Figure 52 is shown with labeled 1.0, 2.03 nm periodicities in the [11-1] direction and 39.1 and 78.1 nm periodicities in the [1-10] direction.
4.5 **LEED of the Si(112)/As surface**

Figures (55-56) are of a LEED image taken at 137 eV of As covered Si(112). The bold box represents the bulk cell while the dotted lines represent the (2×2) reconstructed unit cell. Using the LEED analysis software program, LEEDpat30, as in Section 3.5, a similar fitting can be accomplished with a centered rectangular unit cell with \( a = 0.384 \) nm and \( b = 3.759 \) nm. In Figure 55 the LEED peaks in rows 1, 3, and 5 are matched in the [11-1] direction on a centered rectangle \( a = 0.384 \) nm and \( b = 3.759 \) nm. In rows 2 and 4 the reciprocal lattice points are located between the LEED peaks in the [11-1] direction. All the rows align in the [1-10] direction.

Similarly, in Figure 56, when rows 2 and 4 are matched in the [11-1] direction to the same reciprocal lattice, rows 1, 3 and 5 are located between the peaks in the [11-1] direction. Doubling the lattice constant to \( b = 7.52 \) nm would produce a (1×8) reconstruction of the bulk terminated unit cell for Si(112), where the reciprocal lattice might match well with all the peaks. This was attempted but did not result in observably better results. Figure 57 shows the a) real and b) reciprocal lattices for a centered rectangle with \( a = 0.384 \) nm and \( b = 3.759 \) nm.

When the \( b = 3.759 \) nm of the real centered rectangle lattice is projected by 30° in the (112) plane, 4.34 nm is found or twice the lattice constant for the hexagonal periodicity with \( a' \times 2 = 2.17 \) nm. The same projection for \( b' = 1.889 \) nm equals 2.17 nm as well. This supports the use of an overlaid hexagonal periodicity with \( a' \times 2 = 2.17 \) nm or a Si(111)-like periodicity with \( a = 0.384 \) nm for this surface to help visualize the overall periodicity in the [11-1] direction. The shifting of the matching of the reciprocal lattice from one set of [11-1] rows to another could be due to two or more domains within the coherence length of the LEED experiment.

Notably, the LEED pattern is similar to the LEED pattern from the clean high temperature annealed Si(112) surface discussed in Chapter 3. The centered rectangular unit cells
with \( a = 0.384 \text{ nm} \) lattice constants are identical. The \( b \) lattice constant is slightly different from the high temperature clean annealed \( \text{Si}(112) \) surface. The difference in the LEED patterns for these two surfaces seems to be directly related to the \([11-1]\) direction in the \((112)\) plane.

The ratio of the \( b \) lattice constants for the two surfaces and the ratio of the \( a \) lattice constants for \( \text{Si}(111) \) with \( a = 0.384 \text{ nm} \) and grey arsenic\((111)\) with \( a = 0.413 \text{ nm} \) are equivalent to within 1\% where \( 0.413/0.384 = 1.08 \) and \( \frac{b_{\text{Si}(112)/\text{As}}}{b_{\text{Si}(112)}} = \frac{3.759}{3.516} = 1.069 \). Grey As metal is a graphite analog and the lowest energy allotrope of metal arsenic. The \( \text{Si}(111)-(1\times1) \) and Grey \( \text{As}(111)-(1\times1) \) both form structurally the same honeycomb like planes of atoms with the difference in structure being only their respective \( a \) lattice constants. From the LEED patterns of these two surfaces the 1.08 ratio of the \( b \) lattice constants for centered rectangular unit cell seems to be the main difference in their periodicities.
Figure 55. A LEED image of Si(112)/As with a software generated reciprocal lattice overlaid (black circles). The LEED peaks in rows 1, 3, and 5 are matched in the [11-1] direction on a centered rectangular unit cell with $a = 0.384$ nm and $b = 3.759$ nm. All the rows align in the [1-10] direction. The LEED image was taken at 137 eV. The white rectangle represents the bulk-terminated unit cell while the dotted lines representing the $(2\times2)$ reconstructed unit cell.
Figure 56. A LEED image of Si(112)/As with a software generated reciprocal lattice overlaid (black circles). The LEED peaks in rows 2 and 4 are matched in the [11-1] direction on a centered rectangular unit cell with $a = 0.384$ nm and $b = 3.759$ nm. All the rows align in the [1-10] direction. The LEED image was taken at 137 eV. The white rectangle represents the bulk-terminated unit cell while the dotted lines represent the (2×2) reconstructed unit cell.
Figure 57. The a) real and b) reciprocal lattices for a centered rectangle are shown. The blue rectangle defines the centered rectangle unit cell with $a = 0.384$ nm, $b = 3.759$ nm and $\phi = 90^\circ$. The green outline shows the primitive oblique unit cell (lower symmetry) with $a_s$ equal to $b_s = 1.889$ nm (red vectors) and $\phi_s = 168.33^\circ$. 
4.6 Si(112)-like hexagonal periodicity with $a = 0.3905$

**Figure 58** is a STM image of a $22 \times 22$ nm region of Si(112)/As as deposited in our system. There are $2.0 \pm 0.05$ nm wide rows in the [11-1] direction running in the [1-10] direction. The rows are not atomically straight or of precisely the same width. Three row layers (height) are apparent, dark red being the lowest and bright yellow being the highest. **Figure 58**, Feature a) indicates corrugations with a period of $0.78 \pm 0.01$ nm in the [1-10] direction and $0.25 \pm 0.02$ nm in height are observed. Specifically for Feature a) there are twelve $0.78$ nm period corrugations in the [1-10] direction. Other similar corrugations running in the [1-10] direction with a period of $0.78$ nm in integer multiples of four to twelve $0.78$ nm units, can be observed in the image mixed with areas of apparent disorder. The arrangement of the surface atoms has an appearance of some ordering, probably due to the Si(112) surface. **Figure 59** is a rotated 3D perspective of **Figure 58**. It is shown to highlight the layering of the rows and the mix between the ordered and disordered regions.

**Figure 60** is a zoomed image of Si(112)/As with a Si(111)-like hexagonal periodicity with $a = 0.3905$ nm and a hexagonal periodicity with $a_{x2} = 0.781$ nm overlaid, both oriented in the [1-10] direction. The Si(111)-like hexagonal periodicity matches well to the corrugation in the [1-10] direction as well as the steps in the [11-1] direction. If one considers the layers, the width of the rows are mostly 6 units of the Si(111)-like hexagonal periodicity with $a = 0.3905$ nm, projected over the (112) plane at 30° or $a_{x_{6R30}} = 2.03$ nm in the [11-1] direction. Also, $2.03$ nm is equal to $(3 \times 0.781 \times \cos(30))$ the hexagonal periodicity with $a_{x2} = 0.781$ nm. This second hexagonal periodicity with $a_{x2} = 0.781$ nm fits the hexagonal nature of the arsenic layer in the [1-10] direction. The $2.03$ nm periodicity in the [11-1] direction matches that found for the clean high temperature annealed Si(112) surface discussed in Chapter 3.4-5.
This strongly supports the explanation that the arsenic layer is deposited on the high temperature Si(112) surface and is ordered by that same surface which can be described by multilayer hexagonal periodicity. This would also be described as a moiré pattern.
Figure 58. This figure is a zoomed (22 × 22 nm) STM image of Si(112)/As. The surface was imaged at a bias = 2.0 V and a set point of 0.05 nA. The Z amplitude = 0.77 nm. Feature a) marks a line of corrugation with a period of 0.78 nm in the [1-10] direction and 0.25 nm in height. Specifically for this feature, there are twelve 0.78 nm periods for corrugations in the [1-10] direction.
Figure 59. A 3-D perspective of the image shown in Figure 58.
Figure 60. This figure is a zoomed (22 × 22 nm) STM image of Si(112)/As. The surface was imaged at a bias of 2.0 V and a set point of 0.05 nA. The Z amplitude = 0.77 nm. Dual hexagonal periodicities are overlaid, a Si(111)-like hexagonal periodicity with $a' = 0.3905$ nm and a hexagonal periodicity with $a'_{\perp} = 0.781$ nm, both oriented in the [1-10] direction.
4.7 Two surfaces overlaid

In this section the STM images of two sample surfaces are compared and carefully overlaid. The first STM image in Figure 61 is of the surface described in Chapter 3.5. This surface was prepared by a clean 1200$^\circ$C high temperature anneal of Si(112). The STM image (57.1 $\times$ 57.1nm) with a Z amplitude of 1.0 nm was imaged at a bias of 1.8 V and set point of 0.05 nA. The second STM image in Figure 62 is of the Si(112)/As surface. The STM image (61.2 $\times$ 61.2 nm) with a Z amplitude of 2.24 nm was imaged at a bias of 2.0 V and set point of 0.05 nA. For the multicolor representation of the height in the second image, the colors from dark red to dark yellow span a height range of 1 nm.

Dual hexagonal periodicities with $a_{x2}'' = 2.17$ nm and $a_{x6}' = 2.343$ nm are overlaid parallel to the [1-10] direction in each image. These lattice constants have been chosen from the results of the LEED and FFT analysis discussed earlier in this chapter. The hexagonal periodicity with $a_{x2}'' = 2.17$, when projected over the (112) plane at 30$^\circ$, produces periodicity in the lines generated parallel to the [1-10] direction of 1.88 nm in the [11-1] direction showing the $\times2$ distance of the bulk-terminated Si(112) surface. The second hexagonal periodicity with $a_{x6}' = 2.343$ nm is Si(111)-like with $a = 0.3905$ nm (6$\times$6). In this representation, the hexagonal periodicity overlays show two things. First and primarily, the lines of the dual hexagonal periodicity running in the [1-10] direction form a pattern in the [11-1] direction that fits well to the pattern formed by surface rows in the [11-1] direction. This indicates an ordered relationship between the two hexagonal periodicities in the [11-1] direction similar to what is described earlier for the clean high temperature annealed Si(112) in Chapter 3.5. Second, by using the overlay as a metric, the two images can be adjusted to equal scale and orientation for the overlaying of the two images.
The point of overlaying these two images is to demonstrate how the rows in the [11-1] direction for both images and their hexagonal periodicity overlay after correction where aligned. It becomes apparent during this process, when overlaid many of the larger surface features in both images are aligned.

Using GIMP 2.0 image editing software, the two images are overlaid after scaling and rotating as shown in Figure 63 c) and d). Figure 63 a) and b) are 3D perspectives. The image in Figure 64 is of the layered images with the overlaid Si(112)/As image at 25 % transparency. Figure 65 is a set of 4 images with decreasing transparency in the Si(112)/As layer: a) 100% transparency for the Si(112)/As overlay, b) 75%, c) 50% and d) 25%. The black arrows point to regions or surface structures where the topography of the two surfaces is similar. The spatial relationships on the surface, dimensions of the structures, and their orientations are clearly similar. These STM images are from two different Si(112) wafers.
Figure 61. This is a STM image (57.1 × 57.1nm) of a clean 1200 C° annealed Si(112) surface. Dual HPs are overlaid, with $a''_{x_2} = 2.172$ and $a'_{x_6} = 2.343$ nm. The surface was imaged at a bias = 1.8 V and a set point of 0.05 nA. The Z amplitude = 1.0 nm.
Figure 62. This figure is a STM image (57.1 × 57.1nm) of a Si(112)/As surface. Dual hexagonal periodicities are overlaid, with $a''_{x2} = 2.172$ and $a''_{x6} = 2.343$ nm. The surface was imaged at a bias = 2.0 V and a set point of 0.05 nA. The Z amplitude = 2.24 nm.
Figure 63. In this figure, two 3D perspectives of the STM images of the two sample surfaces. a) Si(112)/As and b) Si(112) are shown. The images in c) Si(112)/As and d) Si(112) are 2D images, showing the rotation about the [112] direction to match the surfaces.
Figure 64. The tan STM image is of a clean annealed Si(112) surface from Figure 61. The multicolored STM image overlaid after graphical manipulation, is that of a monolayer of arsenic deposited on Si(112) from Figure 62 in our lab by MPL’s deposition procedure.
Figure 65. These are four composite images of the images from Figures (61,62) with varying transparency in the overlaid STM image of the Si(112)/As surface: a) 100% transparency for the Si(112)/As overlay, b) 75%, c) 50%, and d) 25%. The black arrows point to specific points where the topography of the two surfaces as compared in the overlay of the two images are similar.
4.8 Discussion

On first inspection, the two surfaces from section 4.7, the high temperature annealed Si(112) and the Si(112)/As, are not similar. Remarkably, after scaling, rotation about the [112] direction, overlaying the two images, and translating the images in the (112) plane, the topological similarity is more than striking. This is not only a qualitative comparison but a quantitative geometric result. The distances and angles in the STM images are preserved during the manipulation of the STM images.

While one or two concurrences in the superimposed images might be probable in two random surfaces, concurrences would not be expected or easily observed. It is therefore reasonable to conclude that the clean high temperature annealed Si(112) surface is representative of the surface that the arsenic adlayer is deposited on.

There are several implications of this result. When one images surfaces with STM, it has been observed that after acquiring a first image and withdrawing the tip away from that point on the surface you can not then return the tip back to that same point and obtain an image of the same area. The variation in the movement of the tip is too large when compared to the area of the image; this is certainly true for the McAllister STM used for these experiments. With surfaces such as Si(111)-(7×7), the repeating nature of the unit cells and large areas they normally cover, allows for imaging similar surfaces regardless of where the tip is centered. If the clean high temperature annealed Si(112) surface has a hexagonal periodicity with $a = 78.1$ nm as concluded in Chapter 3.5, then imaging this surface for an area $60 \times 60$ nm will show 60% of one unit cell. If these unit cells are repeating over the surface, then a second different imaged region would also show 60% of one unit cell. The portions of two images overlaid and translated in the (112) plane should correspond at some point if long range ordering of the atoms within the
superlattice is also present. This seems to be true in this case for these two surfaces. A Si(111)-like hexagonal periodicity with \( a' = 0.3905 \text{ nm} \) that forms a superlattice with a lattice constant of \( a = 78.1 \text{ nm} \) contains \( 3.4 \times 10^4 \) atoms. The existence of this many atoms ordered in a superlattice is an extraordinary conclusion. As demonstrated in Chapter 3.5, imaging these surfaces on areas of \( 40 \times 40 \text{ nm} \) or less will produce a disordered appearance at first inspection but can be matched to a moiré pattern.

The LEED patterns and their unit cells from these two surfaces are both centered rectangular. In the \([1-10]\) direction the lattice constants are identical at \( a = 0.384 \text{ nm} \) and in the \([11-1]\) direction and the \( b = 3.516 \text{ and } b' = 3.759 \text{ nm} \) constants differ by five percent. It is clear that a major portion of the inverse unit cell at \( 0.01281/\text{nm} \) would be unobservable with our LEED experiments due to the position on the screen of the electron gun. The similarities of the two LEED patterns argue for the same level of similarities in the surfaces.

X-ray-scattering results also support the large superlattice unit cell. Mochrie’s et al.(4) results show a periodicity of \( 67.0 \pm 1.5 \text{ nm} \) in the \([11-1]\) direction for the for the Si(112) surface at temperatures between \( 866^\circ \text{C} \) and \( 882^\circ \text{C} \). A hexagonal periodicity, where one lattice vector of the hexagonal lattice is parallel to \([1-10]\) and the other \( 30^\circ \) from \([11-1]\) on the Si(112) surface, with a lattice constant of \( a = 78.1 \text{ nm} \), has a projected periodicity at \( 30^\circ \) of \( 67.6 \text{ nm} \) in the \([11-1]\) direction. There is also long range periodicity (>60 nm) in the \([1-10]\) direction as shown in Chapter 3.4.

The annealing and arsenic deposition step on Si(112) for MBE growth of Si(112)/As/ZnTe/CdTe thin films can be described with these new insights into the two surfaces. After RCA cleaning a sample of Si(112), the surface has multiple layers of oxide. During the ramp up in temperature the oxide is removed. The oxides layer’s presence stabilizes
the Si atoms at the interface between the Si-bulk and silicon oxide layer so that restructuring does not occur as the temperature increases to 950° C. Once the sample temperature is greater than 900° C and all the oxide is removed, the sample restructures into the high temperature surface observed for the clean high temperature Si(112) surface in section 3.5. Before ramping down, the temperature to 400° C, the arsenic flux is turned on. An arsenic monolayer is deposited on the high temperature Si(112) surface. The arsenic monolayer stabilizes the silicon surface as it is cooled down preventing the restructuring and faceting in the lower temperature ranges (< 839° C) from occurring. At 400° C the surface we observed with STM for Si(112)/As is present. Without the arsenic monolayer on the Si(112) surface, as the sample cools restructuring and faceting occurs resulting in significantly more defects in the subsequently grown MBE thin film.

A significant amount of time and effort was spent attempting to match the arsenic atoms to the bulk- terminated Si(112) single crystal surface, and its (1x2), and (2x2) unit cells to the STM images of Si(112)/As without success. A repeating unit cell lattice-matched to the Si(112) surface was not determined. The modeling was done with Cerius2 and Chemdraw software and at times a large number of atomic modeling kits.
4.9 Conclusions

After a monolayer of As is deposited on clean, annealed Si(112) surfaces, distinct rows, 2.0 nm wide in the [11-1] direction and running parallel to the [1-10] direction, are observed with STM. STM images of local regions of the Si(112)/As surface demonstrate a Si(111)-like hexagonal periodicity with $a' = 0.3905$ nm. In these regions, the corrugation height along the rows in the [1-10] direction is 0.25 nm. The LEED image of Si(112)/As can be fitted with a centered rectangular unit cell, with $a = 0.384$ nm and $b = 3.7586$ nm, which is similar to the clean high temperature annealed Si(112) surface in Chapter 3.5. Nanofaceting of the Si(112)/As surface is not observed. The arsenic monolayer suppresses the faceting as the sample is cooled during the annealing step. STM images of the high temperature annealed Si(112) and the Si(112)/As surface can be superimposed with strong correlation. When deposited by MBE at temperatures above 950° C, the arsenic monolayer preserves the high temperature annealed Si(112) surface with a hexagonal periodicity of $a = 78.1$ nm as the surface is cooled to room temperature.
Appendix A  Chemical preparation

This is the RCA process used for cleaning samples before introduction into the analysis chamber. It is important to understand that all of these silicon surfaces are received with a large surface oxide layer and chemical impurities. The RCA process removes the impurities from the surface of the wafers and imparts a 3.0 nm thick oxide layer at the surface. The modified RCA process we use for wafer cleaning is as follows:

Wafer cleaning chemical oxygen cleaning procedure

Duration:  Approximately 1 hour

Purpose:  Preparation of silicon wafers for the UHV cleaning anneal. Ideally, all foreign matter is removed from the surface and then chemically prepares a SiO₂ layer that is 1.0 to 3.0 nm thick.

Materials:  Ammonium hydroxide 29% solution.

Hydrochloric acid 37% solution.

Hydrofluoric acid 49% solution.

Polished Epi-ready silicon wafer

5:1:1 volumes: 500 mL : 120 mL : 120 mL

Equipment:  1 ceramic beaker – 1 L

9 Pyrex beakers -- 1 L.

Fluoroware Substrate Holder (per wafer)

1 Fluoroware Thong

Hotplate

N₂ gas
Procedure:

1. Prepare a 5:1:1 solution of $\text{H}_2\text{O} : \text{NH}_4\text{OH} : \text{H}_2\text{O}_2$. (Referred to as ammonium hydroxide solution or AHS.)

2. Clean all beakers and tools with heated ($80^\circ$ C) AHS

3. Thoroughly rinse all tools in beakers with de-ionized water

4. Prepare AHS and heat to $80^\circ$ C

5. Place silicon wafers in AHS solution for 20 to 30 minutes.

6. Prepare a 5:1:1 solution and $\text{H}_2\text{O} : \text{HCl} : \text{H}_2\text{O}_2$. (Referred to as hydrochloric solution or HCS.)

7. Begin heating HCS to $80^\circ$ C

8. Prepare 5% by volume solution of HF

9. Rinse wafers in 7 consecutive baths of 900 mL of de-ionized water

10. Rinse wafers in HF solution

11. Place wafers in HCS solution for 12 minutes

12. Rinse wafers in 13 consecutive baths of 900 mL of de-ionized water

13. Dry wafers with nitrogen gas. Dry wafers from top to bottom pushing excess water away from you.

   
   a. During the entire disposal process keep de-ionized water running in sink

   b. Wait for AHS and HCS solutions to cool to room temperature before disposing. (See note 1)
c. Transfer HF solution to a clearly labeled HF hazardous waste container.

d. Pour AHS into a base waste container (8.22 pOH) (See note 1, 2)

e. Pour HCS into an acid waste container (5.68 pH) (See note 1, 2)

f. Always return containers to the appropriately labeled hazardous waste cabinet.

Note 1:
AHS and HCS disposal are in compliance with the citation 40 CFR 403.5(b)(2) and Chicago Water Reclamation District Sewer use ordinance, Appendix B, Section 1

(See Appendix A,B,C of this document).

Note 2:
If there is any mercury contamination of any solution, these solutions must be disposed of in a properly labeled waste container and not poured down the drain.

(See Chicago Water Reclamation District Sewer use ordinance, Appendix B, Section 1. Subsection I, Appendix A of this document.)
5. CITED LITERATURE


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Chou, HA., Zavitz, D.H., Ovadia, M. *In vivo CH3(CH2)11SAu SAM electrodes in the beating heart: In situ analytical studies relevant to pacemakers and interstitial biosensors*. Biosensors & Bioelectronics 2003;18(1), 11-21


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**ABSTRACTS AND PRESENTATIONS**


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**PROFESSIONAL AFFILIATIONS**

American Chemical Society
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