PHOTOEMISSION STUDIES OF INTERFACE EFFECTS ON
THIN FILM PROPERTIES

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Abstract

As the thickness of a metallic film decreases to the atomic scale, the confinement of the film's electrons by its boundaries gives rise to discrete electronic states, known as quantum well states, which dominate the film properties. This work investigates the use of film-substrate boundary modification as a means to control the film properties through the manipulation of its quantum well states. Specifically, the Schottky barrier heights and thermal stability temperatures for Pb(111) films grown on metal-reconstructed Si(111) substrates are shown to be determined by the interfacial conditions produced by the various Si-terminating metals (Au, Ag, In, and Pb), known as interfactants.

These properties are probed experimentally with angle-resolved photoemission spectroscopy using vacuum ultraviolet synchrotron radiation. An analysis of the measured quantum well energy levels and peak widths determines the height of the Schottky barrier, the rectifying energy barrier at a metal-semiconductor junction. A calculation based on the known interface chemistry and the electronegativity yields predicted barrier heights in good agreement with the experiment. These results demonstrate that the Schottky barrier height can be tuned to a desired value through an appropriate selection of interfactant.

Extending the exploration of interfactant effects to physical properties, the thermal stability temperatures of Pb films are measured with photoemission. The quantized electronic structure in Pb films causes the thermal stability to oscillate with an approximate bilayer period. A comparison among the systems reveals a phase reversal and an amplitude deviation in the stability temperatures. For Pb/In-$\sqrt{3}$×$\sqrt{3}$/Si(111), films made of odd numbers of atomic layers are observed to be more stable than the even ones, but this trend is reversed for the other cases studied. For Pb/Au-6×6/Si(111), the maximum stability temperatures are in excess of room temperature, unlike the other systems. These results show that the temperature-dependent thermal stability behaviors can be controlled by interfacial engineering.
To Vin, because I owe it to you.
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## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ARPES</td>
<td>Angle-resolved Photoelectron Spectroscopy, or Angle-resolved Photoemission.</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled Device.</td>
</tr>
<tr>
<td>EDC</td>
<td>Energy Distribution Curve.</td>
</tr>
<tr>
<td>( fcc )</td>
<td>Face-centered Cubic.</td>
</tr>
<tr>
<td>FM</td>
<td>Frank-van der Merwe.</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic Energy.</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular Beam Epitaxy.</td>
</tr>
<tr>
<td>MCP</td>
<td>Micro-channel Plate.</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer.</td>
</tr>
<tr>
<td>NIM</td>
<td>Normal Incidence Monochrometer.</td>
</tr>
<tr>
<td>PGM</td>
<td>Plane Grating Monochrometer.</td>
</tr>
<tr>
<td>SBZ</td>
<td>Surface Brillouin Zone.</td>
</tr>
<tr>
<td>SK</td>
<td>Stranski-Krastanov.</td>
</tr>
<tr>
<td>TSP</td>
<td>Titanium Sublimation Pump.</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh Vacuum.</td>
</tr>
<tr>
<td>U-NIM</td>
<td>Undulator Normal Incidence Monochrometer.</td>
</tr>
<tr>
<td>VBM</td>
<td>Valence Band Maximum.</td>
</tr>
<tr>
<td>VW</td>
<td>Volmer-Weber.</td>
</tr>
<tr>
<td>XTM</td>
<td>Crystal Thickness Monitor.</td>
</tr>
</tbody>
</table>
List of Symbols

\( \chi \) Chemical electronegativity measured on the Mulliken scale.
\( \chi_S \) Semiconductor electron affinity.
\( \Delta N \) Period of thickness oscillations in monolayers.
\( \lambda \) Mean free path.
\( \lambda_F \) Fermi wavelength.
\( \Phi \) Thermal stability oscillation phase factor.
\( \phi_i \) Electronic phase shift at film-substrate interface.
\( \phi_M \) Metal work function.
\( \phi_s \) Electronic phase shift at film-vacuum surface.
\( a \) Lattice constant of conventional unit cell.
\( C \) Terminating metal coverage as a fraction of surface site density.
\( E \) Quantum well state energy.
\( E_0 \) Energy confinement range.
\( E_F \) Fermi energy.
\( E_g \) Semiconductor energy gap.
\( h \) Planck’s constant, equal to \( 6.626\times10^{-24} \) m²kg/s.
\( h\nu \) Photon energy.
\( k \) Wave vector of electron momentum.
\( k_F \) Fermi wave vector.
\( k_{||} \) Wave vector of parallel momentum.
\( k_{\perp} \) Wave vector of perpendicular momentum.
\( N \) Film thickness in monolayers.
\( N_A \) Avagadro’s number, \( 6.022\times10^{23} \) mol\(^{-1}\).
\( n \)  Quantum number used in layer-resolved quantum well studies.

\( p \)  Alternate quantum number used in non-layer-resolved quantum well studies.

\( Q \)  Interface charge parameter.

\( S \)  Schottky barrier height.

\( t \)  Film thickness in Angstroms.
The atomic world is the current frontier of technological innovation, possessing possibilities that have only begun to be explored. Prospective medical therapies hinge on the manipulation of individual biomolecules; sub-micron particles are employed for chemical delivery and mechanical versatility. In no field has operational size reduction been more significant than that of electronics. The length scale of the transistor, the fundamental unit of solid-state electronics, has decreased by five orders of magnitude over the sixty years since its creation. This physical miniaturization of device components, and subsequent increase in efficiency, data storage capacity, and processing speed, produced the foundation for the prevailing information age. Current endeavors to build upon these advances have propelled us to the nanoscale threshold.

As technology continues its relentless march to the atomic level, it enters the strange realm of quantum behavior. When systems possess length scales on the order of the electron coherence length, non-classical behaviors can emerge. These quantum properties deviate sharply from those observed on the macroscopic level where most existing technologies are designed to operate. As electronic device miniaturization descends further toward the atomic realm it becomes increasingly imperative to comprehend the quantum physics that dominates the regime in order for technological progress to continue.

Thin films are the basic building blocks for solid-state devices, and their simple geometry makes them ideal models for fundamental studies as only one of their three spatial dimensions has a length scale in the quantum regime. This broad expanse and narrow depth permits ultraviolet angle-resolved photoemission, the technique described in Chapter 2, to be a probe well-suited to the study of the thin film electronic structure. When the thickness of a film decreases to the atomic scale, the confinement of the film’s electrons in one dimension by its boundaries quantizes the film band structure perpendicular to the surface and gives rise to discrete electronics states. As discussed in Chapter 3, these quantum well states are highly responsive to changes in film thickness and boundary conditions. This property allows
the “surface sensitive” technique of photoemission to be used in a novel manner to probe the effect of buried interfaces. Quantum well states cause the electronic and physical film properties to drastically differ from those of bulk systems. Controlling these characteristics at a quantum level is critical for thin film applications and is the subject of this research. Specifically, we explore the modification of the boundary condition as a means to deterministically alter such properties as the Schottky barrier and the thermal stability of thin films.

This work is an angle-resolved photoemission study of ultrathin Pb films grown on several interfactant-terminated Si(111) surfaces. This particular metal-on-semiconductor system was selected for several reasons. Lead is a prototypical free-electron-like metal whose films have been predicted and observed to be strongly influenced by quantum size effects. Single-crystal silicon has been extensively studied, is easy to prepare, and is ubiquitous in semiconductor device applications. The two elements do not intermix and so the Pb-Si interface is abrupt, a necessary condition for producing smooth films with well-defined boundaries. Metal interfactant layers are introduced to the system by reconstructing the Si(111) surface with various metals, including Ag, Au, In, and Pb, prior to the deposition of the Pb overlayer. By maintaining the same film and substrate while varying the interfactant, we have isolated the interface effect on the film properties.

The Schottky barrier is the rectifying energy barrier that forms at the junction between a metal and semiconductor. It is an important feature of solid-state electronics because it determines the transport properties of the interface and the quantum well electronic structure of the film. The origin of the Schottky barrier and the determination of its height have been issues of long-standing interest. While originally postulated to arise solely from the bulk properties of the system, more recent experiments have suggested that the barrier height also depends strongly on the metal-semiconductor interface. Chapter 4 describes an experiment that probes this conjecture, demonstrating that the Schottky barrier height depends on the interfacial chemical composition. Quantum well spectroscopy is used to determine the Schottky barrier for several interfactant systems, extracting the barrier height from measurements of the quantum well energies and peak widths over a range of film thicknesses. An analysis of the results establishes that a simple chemical model, whose only parameters are the electronegativity and concentration of the metal used for Si termination, can describe the interface component of the Schottky barrier height. The implication of these findings is that it is possible to tune the Schottky barrier to a desired height through
the judicious selection of a metal interfactant.

The thermal stability temperature of a film is the threshold annealing temperature at which the film’s structure begins to roughen. This physical parameter is relevant to the film’s robustness under technological application operating conditions. Previous work on the Pb film system has shown that its thermal stability temperature, like many of its physical properties, oscillates as a function of thickness due to variations in the total electronic energy of the film. Extending the technique of quantum well spectroscopy to examine the interface effect on film thermal stability reveals that the phase and amplitude of these oscillations can be manipulated with interfactants. The results presented in Chapter 5 demonstrate that interfacial engineering can also be used to exert control over thin film physical properties.

This body of work, taken as a whole, illustrates the relationship between film electronic structure and physical properties and their sensitivity to the boundary condition. These findings offer significant insight into and predictive power about the basic atomic-level physics that are important to the future of thin film technological applications.
2 Photoemission Spectroscopy

2.1 Introduction

Photoemission is the process in which a photon incident upon a system excites a bound electron to an unbound, unoccupied state. If this photoelectron escapes the system, the measurement of its momentum and kinetic energy can be used as a spectroscopic technique for probing the electronic structure of the system [1–5]. Photoemission spectroscopy currently serves as a common method for mapping the band structures of solids, but due to its inherent surface sensitivity it did not become a viable tool until the 1960’s with the advent of ultrahigh vacuum systems. The technique’s origins lie in the photoelectric effect, which was first observed in 1887 by Heinrich Hertz. In this phenomenon, a metal surface irradiated by ultraviolet light emits electrons, as shown in Figure 2.1. Albert Einstein later explained the photoelectric effect as a quantum behavior governed by the relationship

\[ KE_{\text{max}} = h\nu - \Phi \]  

(2.1)

between the maximum kinetic energy \( KE_{\text{max}} \) of the photoelectrons, the photon energy \( h\nu \), and the work function \( \Phi \) of the emitting solid. The work function is the minimum energy needed to excite an electron from the solid into the vacuum. The photoelectric effect was eventually shown to be a simplified case of the more general photoemission process.

2.2 The Photoemission Process

Electrons in a solid occupy bound states of the system’s electronic structure. If an electron excited from an initial state of binding energy \( BE \) by a photon with energy \( h\nu \) overcomes the solid’s work function \( \Phi \), it will possess a kinetic energy \( KE \) in the vacuum

\[ KE = h\nu - \Phi - BE, \]  

(2.2)
Figure 2.1: Schematic depiction of photoemission. As concisely described by many scientists: “Photons in, electrons out.”

as illustrated in Figure 2.2. The binding energy is typically referenced to the sample Fermi level. When an electron at the Fermi level of a metal is photoexcited, as in the photoelectric effect, Equation (2.2) reduces to Equation (2.1). At a given photon energy, photoemission spectroscopy can measure electrons from states of energies within \( h\nu - \Phi \) of the Fermi level. Increasing the photon energy allows more tightly-bound states to be probed.

It should be noted that under experimental conditions the kinetic energy of the photoelectron is not measured in vacuum, but rather in an electron energy analyzer. These kinetic energies are not equivalent because the sample and the analyzer do not have identical work functions. In most experiments, the sample and the analyzer are grounded to align their Fermi levels. As shown in Figure 2.2, this ensures that the sum \( KE + \Phi \) in the analyzer, and thus the measured binding energy, is the same as in the sample.

Electrons emitted into the vacuum behave as free electrons with momentum components perpendicular \( (\hbar k_\perp) \) and parallel \( (\hbar k_\parallel) \) to the sample surface. In the normal emission geometry, electrons are emitted perpendicular to the surface with no parallel momentum component. Conversely, off-normal photoelectrons possess a non-zero parallel momentum. When an electron passes out of a solid into the vacuum, the parallel component of its momentum is conserved (to within a surface reciprocal lattice vector), but not its perpendicular component, much like the refraction experienced by
Figure 2.2: Energetics of the photoemission process. The equivalence of the sample and analyzer Fermi levels induced by grounding allows for the accurate measurement of the state binding energy.

light when it passes through the interface between two different media. In an experiment, the parallel momentum is derived from the measured electron kinetic energy and its emission angle $\theta$ from the surface normal. Given that the kinetic energy of a free electron in the vacuum is

$$ KE = \frac{\hbar^2}{2m} k^2, \quad (2.3) $$

the wave vector corresponding to the electron parallel momentum is

$$ k_{||} = \sin \theta \sqrt{\frac{2m}{\hbar^2} KE}. \quad (2.4) $$

The conservation of parallel momentum requires the detected $k_{||}$ to be the same as that of the initial electron state within the solid. If $k_{||}$ is oriented along a high symmetry direction of the sample, the system band structure can be constructed by pairing $BE$ measurements with those at correlated $k_{||}$. Angle-resolved photoelectron spectroscopy (ARPES), in which the electron analyzer has a high degree of angular $\theta$ resolution, makes possible the experimental determination of a system’s dispersion relationships $E(k_{||})$. Determination of $k_{\perp}$ is a more complicated issue that often involves taking spectra at many different photon energies.
The energy and momentum, along with angular symmetry and spin, form the set of quantum numbers that define the initial bound state of an electron in a solid characterized by a periodic crystal lattice [4, 5]. The final state to which an electron can be excited is constrained by the transition cross section with the quantum numbers adhering to the selection rules it implies. In addition to the energy and momentum relations previously discussed, spin is also conserved. The state symmetry depends on the polarization \( \lambda \), which enters the process through the photon field vector potential \( A \). The photoemission transition cross section is given by an expression of the Fermi “golden rule” variety in which the Hamiltonian is

\[
H = \frac{(p - A)^2}{2m} = \frac{1}{2m}(p^2 - 2A \cdot p + A).
\]  

This is a transverse gauge transformation of the momentum operator \( p = -i\hbar \nabla \) by the vector potential, which for a plane wave is \( A = \alpha \lambda e^{i \mathbf{k} \cdot \mathbf{r}} \). For the photons used in ultraviolet photoemission, \( k \) is on the order of \( 10^7 \) m\(^{-1}\). The size of an atom (10\(^{-10}\) m) is the relevant length scale, so the exponential term approximates to unity. The presence of \( \lambda \) in the \( A \cdot p \) cross term creates a polarization dependence. Photoemission intensity variations emerge if the orientation of the sample changes relative to the photon polarization. The \( A^2 \) term is constant and its zeroth-order contribution to the transition cross section can be neglected.

### 2.3 Surface Sensitivity

Photoemission spectroscopy is notable for its surface sensitivity, a characteristic that is both a strength and a weakness. It allows the technique to discriminate and identify surface-related electronic states, but it also restricts the method to studying electrons that are physically close to the surface. This limitation can impede studies of buried interfaces and bulk states. Photons have no trouble penetrating crystal samples, but the short mean free path of photoelectrons limits the probe depth. The mean free path is the average distance travelled by an electron through the sample before it scatters. If a photoelectron scatters before it reaches the vacuum, it loses information about its initial state. Figure 2.3 displays a plot of the experimental mean free path of electrons as a function of their kinetic energy [6]. This is often referred to as a “universal” curve because the relationship is measured to be about the same for electrons in various elemental crystals. Electrons penetrate solids further at higher kinetic energies, but their mean
free path also increases at very low energies because they are too weak to excite plasmons or a large number of electrons, thus producing the distinctive “U” shape of the curve. Varying the photon energy adjusts the electron kinetic energy and permits the degree of surface sensitivity to be tuned, with the minimum of the curve, between 30 and 70 eV, as the most sensitive. Photoemission, however, is not completely blind to deeper structures. If, through their wave nature, near-surface electrons couple to underlying features, then information about these buried states can be accessed.

2.4 Photoemission Spectra

An experimental photoemission spectrum, such as that in Figure 2.4, consists of a plot of the photoelectron count versus electron kinetic energy collected at a specific photon energy and angle relative to the sample normal. Also known as an energy distribution curve (EDC), the spectrum is dominated by three types of features: a sharp cutoff, peaks, and a background [5].

The cutoff in detected intensity indicates the Fermi level of the sample. It is not ideally sharp, with a small number of counts populating the region above the actual Fermi level, due to the finite temperature at which experiments are executed. By fitting the cutoff with a standard Fermi function to
determine $E_F$ in kinetic energy and then resetting the origin at the Fermi level, the photoemission spectrum can be scaled in terms of binding energy. If there is no electron population at the Fermi level, such as when $E_F$ falls within a semiconductor band gap, then no cutoff will be observed in the spectrum. It should be noted that in this case the unoccupied “Fermi level” is the system chemical potential.

Occupied states in the sample electronic structure, such as core level and valence states, appear as peaks. Core level states arise from electrons in closed shells that are tightly bound to individual atoms. They possess large binding energies and, consequently, appear at small kinetic energies. In contrast, valence states involve weakly bound outer shell electrons whose wave functions extend to and interact with neighboring atoms. Valence electrons are involved in bonding and, under the influence of a crystal lattice, their states compose the band structure of solids. Due to their weak atomic binding, valence states lie in close proximity to the Fermi level and, for a given photon energy, appear in spectra at relatively higher kinetic energies than core level states.

Core electrons are heavily shielded by valence electrons of the same atom. The observation of core level peaks can be used to identify the presence of particular atomic species on the sample surface. When valence electrons are involved in bond formation, the orbital rearrangement alters the screening effect and changes the core level binding energy by up to several electron
volts. While numerous photoemission studies have focused on measuring the chemical shifts of core level peaks, the requisite deconvolution and disambiguation can be non-trivial.

Both bulk and surface state peaks can be found in the valence band region. Bulk states are standard Bloch waves that oscillate within the bulk crystal and decay into the vacuum [7]. Surface states, however, have their amplitude localized around the surface and their wavefunctions decay into the bulk as well as the vacuum, as contrasted in Figure 2.5. The surface of a solid differs from its bulk crystal due to its disparate atomic and symmetric environment, often leading to valence band energy levels that are decoupled from the bulk. These states can arise from surface reconstructions, adsorbate bonding, and even the symmetry broken by the truncation of the bulk lattice. Surface states exist in the bulk band gap and their symmetry reflects the surface, not the bulk, periodicity. The two dimensional nature of surface states allows them to be distinguished from their bulk counterparts. Unlike bulk states, which disperse in all three dimensions, surface states are localized relative to the surface normal direction. Although surface state peaks disperse with changing $k_{||}$, they remain constant with respect to the variations in $k_{\perp}$ that are affected by altering the photon energy, as in Figure 2.6(a) [8]. Surface states can also be identified by their sensitivity to chemisorption. Contamination interferes with the physical features that give rise to surface states, thus suppressing or altering their characteristic peaks. Figure 2.6(b) demonstrates how this sensitivity allows surface states to be used to monitor sample quality [9].

A photoemission spectral peak would ideally have a Lorentzian lineshape centered on the state’s binding energy, with the peak width corresponding to the lifetime of the photoexcited state [5]. In practice, the experimentally measured peak is broadened by finite instrumental resolutions, thermal effects, and sample disorder. Analytically this is accounted for by modelling the peak with a Lorentzian convoluted with a Gaussian, where the sources of error add in quadrature to compose the Gaussian width. This distribution is referred to as the Voigt lineshape

\[
G(x, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{x^2}{2\sigma^2}}
\]

\[
L(x, \gamma) = \frac{\gamma}{\pi} \frac{1}{x^2 + \gamma^2}
\]

\[
V(x, \sigma, \gamma) = \int_{-\infty}^{\infty} L(u, \gamma) G(x - u, \sigma) du
\]
which, while it does not have a closed-form representation, can be approximated numerically [10]. Peaks near the Fermi level will also be affected by the cutoff function. If a state lies just below $E_F$, it will appear truncated and asymmetrical as in Figure 2.7. If a state lies just above $E_F$ and is thermally populated, a cut-off segment of its tail will appear as a weak peak centered at the Fermi level.

The spectral peaks sit on a background of counts that increases with decreasing kinetic energy. The background arises from inelastically scattered electrons. For valence spectroscopy, the main contribution is a tail of secondary electrons caused by energy losses to electron-hole pairs. In the near-Fermi level region, this background can be modelled as a polynomial function in electron energy. All three classes of primary features - peaks, background, and the Fermi cutoff - must be accounted for simultaneously in order to accurately fit and interpret photoemission spectra during analysis.

### 2.5 Photoemission Apparatus

The success of photoemission spectroscopy as an atomic-level scientific probe with respect to these studies rests on, among others, three technological accomplishments: synchrotron radiation, ultrahigh vacuum conditions, and the hemispherical electron energy analyzer.
2.5.1 Synchrotron Radiation

In order to produce a sufficient photoelectron yield from a state with a particular binding energy, photoemission needs a high intensity monochromatic photon source. In particular, valence band spectroscopy requires light at multiple ultraviolet energies due to the electron state energy range it probes and its need to differentiate between surface and bulk states. Among the principal photon sources in use today, modern synchrotron facilities, like the Synchrotron Radiation Center in Stoughton, Wisconsin, where these experiments were executed, are well-suited to meet these requirements.

Synchrotron radiation is light emitted by electrons undergoing centripetal acceleration [11, 12]. Synchrotron facilities feature a storage ring in which the paths of electrons are bent into a quasi-circular trajectory by magnetic fields. When charged particles are accelerated to travel a nonlinear course, they will emit electromagnetic radiation. Under non-relativistic conditions, the radiation will adhere to a simple dipole distribution around the electron, as depicted in Figure 2.8. At relativistic energies, such as the 800 MeV or 1 GeV at which the SRC storage ring operates, the angular distribution of photons is peaked sharply in the direction tangent to the circular path of the electrons. Synchrotron light sources have an extremely high flux due to this disproportionate forward distribution.

Synchrotron photons can be filtered and focused by the various beamlines situated around the ring through a combination of electromagnetic

Figure 2.6: (a) Comparison of bulk (sp direct) and surface state behaviors when the photon energy ($k_\perp$) is changed [8]. (b) A surface state is seen to decrease as the concentration of a contaminant increases [9].
fields, mirrors, and diffraction gratings. Figure 2.9 shows an overhead view of the Aladdin storage ring at the Synchrotron Radiation Center. Each beamline is designed to provide intense flux and high energy resolution over particular photon energy ranges. The experiments presented in this thesis were conducted on three of these beamlines: the Undulator Normal Incidence Monochrometer (U-NIM), the Plane Grating Monochrometer (PGM), and the 4-meter Normal Incidence Monochromometer (4-m NIM). The flux-resolution specifications for the U-NIM and the PGM in Figure 2.10 reveal that while the U-NIM is optimized to produce high intensity photons with $\hbar\nu$ between 6 and 30 eV, the PGM possesses a much wider ultraviolet photon energy range. Several other beamlines at the facility are configured to produce the soft x-rays useful for core level studies. Each beamline has a set of entrance and exit slit apertures that can be adjusted to increase photon count at the expense of energy resolution. An essential feature of each beamline is its monochromator, which permits the continuous tuning of photon energy over the optimized range. Other common photon sources, such as helium lamps, x-ray tubes, and lasers, tend to be restricted in range to their discrete inherent emission energies.

To prevent the ambient scattering of the electrons and photons involved in the synchrotron process, and the subsequent loss of energy, resolution, and flux, the storage ring and beamlines operate under ultrahigh vacuum conditions. The photoemission chamber also resides in this low pressure range, allowing for a contiguous, compatible experimental system.
2.5.2 Ultrahigh Vacuum

Photoemission spectroscopy, like all surface science, began to thrive with the attainment of ultrahigh vacuum (UHV) pressures in the laboratory. UHV conditions are those with pressures below $10^{-9}$ torr. The primary purpose of the vacuum is to keep the sample clean and preserve the surface-related properties that contamination would destroy. Given the surface sensitivity of photoemission, sample cleanliness is essential for the technique to be useful.

The rate of contamination depends on the nature of the ambient gas molecules in a system [13]. The behavior of a gas with molecular diameter $d$ and number density $n$ can be expressed through its mean free path

$$\lambda = \frac{1}{\sqrt{2\pi nd^2}}$$

which defines the manner of gas flow for a container of diameter $D$. If the ratio $\lambda/D$ is less than 0.01, then the gas acts as a fluid and intermolecular forces dominate in what is called the viscous flow regime. If $\lambda/D$ is greater than 1, the gas is in a molecular flow regime where collisions are negligible. Between the two extremes is the transitional Knudson regime. Gas molecules in ultrahigh vacuum conditions behave under molecular flow such
that interactions between particles can be neglected in statistical calculations.

The lifetime of a clean sample varies inversely with the rate of contamination, which can be determined through geometry and statistical mechanics [14,15]. The equation of state for collection of non-interacting gas molecules is \( p = nk_B T \), where \( p \) is the average system pressure, \( T \) is the system temperature, and \( k_B \) is the Boltzmann constant. Consider the infinitesimal cylinder above a surface in Figure 2.11, the volume of which is \( dS \, v \, dt \, \cos \theta \) and that contains \( f(v) \, d^3v \) molecules per unit volume with velocities between \( v \) and \( v + dv \). The number of molecules with velocities in this range that strike a unit area of the wall per unit time is

\[
R(v) \, d^3v = d^3v \, f(v) \, v \cos \theta
\]  

2.7
where $f(v)$ is the Maxwell velocity distribution

$$f(v) = n \left( \frac{m}{2 \pi k_B T} \right)^{3/2} e^{-\frac{mv^2}{2k_BT}}$$  \hspace{1cm} (2.8)$$

for particles of mass $m$. Integrating over all of space and expressing the number density in terms of pressure obtains

$$R = \frac{p}{\sqrt{2\pi mk_BT}}.$$  \hspace{1cm} (2.9)
Figure 2.11: Schematic for calculating the contamination rate of a surface due to ambient gas molecules.

The arrival rate varies linearly with the pressure and thus an improvement in the vacuum by a factor of two halves the molecular quantity impinging upon the sample surface. For a gas such as atmospheric nitrogen or carbon monoxide \((m = 28 \text{ amu})\) at a pressure of \(10^{-6} \text{ torr}\), the arrival rate at room temperature is roughly \(4 \times 10^{14}\) molecules per second per square centimeter. If a sample has a typical molar density of \(N_A = 10^{23} \text{ cm}^{-3}\), then its surface density is approximately \((N_A)^{\frac{2}{3}} = 10^{15} \text{ cm}^{-2}\) and every surface site is hit by a gas molecule roughly once per second. A sample surface with a high sticking coefficient will become completely contaminated in one second at a pressure of \(10^{-6} \text{ torr}\), destroying any surface states before they can be probed with photoemission. Experimental necessities require pressures lower than \(10^{-10} \text{ torr}\) so that samples remain uncontaminated for several hours. As seen in Table 2.1, such a pressure falls into the UHV regime.

For a photoemission system to operate at ultrahigh vacuum pressures, it must meet several criteria, of which one is construction from UHV-compatible materials. Minimization of molecular out diffusion, or outgassing, from surfaces under UHV conditions is essential. This precludes the use of high vapor pressure materials like plastics, rubber, and organic lubricants and sealants. Surfaces must also be cleaned of oils, usually accomplished via methanol and acetone rinses, due to their high outgassing rates. The natural oils from a standard fingerprint outgas at a rate of \(1 \times 10^{-5} \text{ torr liters per second}\), which
<table>
<thead>
<tr>
<th>Class</th>
<th>Pressure (torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Vacuum</td>
<td>&gt; $10^{-3}$</td>
</tr>
<tr>
<td>Medium Vacuum</td>
<td>$10^{-3}$ to $10^{-6}$</td>
</tr>
<tr>
<td>High Vacuum</td>
<td>$10^{-6}$ to $10^{-9}$</td>
</tr>
<tr>
<td>Ultrahigh Vacuum</td>
<td>&lt; $10^{-9}$</td>
</tr>
</tbody>
</table>

*Table 2.1: Vacuum range classifications.*

at a pressure of $10^{-10}$ torr would require a pumping speed of 10,000 liters per second to counteract. Photoemission chambers, components, and seals are typically composed of clean metals (stainless steel, copper, aluminum) and insulators (mica, glass, ceramics). These materials have low vapor pressures and their surfaces can be cleaned *in vacuo* by heating them concurrent with pumping. This process, called baking, thermally desorbs molecules off the interior chamber surface into the vacuum where they can be removed through various pumping mechanisms.

The process of lowering a photoemission system from atmospheric pressure, 760 torr, down to the UHV regime requires different pumping mechanisms [13]. As detailed in Figure 2.12, no single class of pumps spans the entire range of pressures and gas flows. For the chamber used in this experimental work, the following course was followed. A standard rotary pump was used to decrease the chamber pressure to the millitorr range, which transformed the gas from the viscous flow to the molecular flow regime. A turbomolecular pump, in which a rapidly spinning bladed turbine compresses the gas and imparts momentum to the molecules such that they are directed out from the chamber toward an exhaust, then lowered the pressure to $10^{-6}$ torr. The rotary pump was run concurrently because the turbomolecular pump can only operate in the molecular flow regime.

An ion pump subsequently decreased the chamber pressure to the UHV range. An ion pump consists of two titanium or tantalum plate cathodes, anodes, and a set of magnets, as shown in Figure 2.13. High voltage creates electrons that ionize gas molecules, which are then held in spiral orbits by the magnetic field until they strike the cathode plate. The ions react with the cathode material, which is ejected and collected on the anode. This process of pumping chemically active gases such as nitrogen, oxygen, and hydrogen from the vacuum is called “gettering”. Inert gases are also removed from the system when they are ionized and subsequently buried in the cathode, but this process is roughly two orders of magnitude less efficient than that for active gases. Secondary pumping is accomplished with a titanium sublimation pump (TSP), which also uses the gettering process.
In a TSP, gas molecules react with a titanium layer on the chamber walls deposited from a heated Ti filament. By pumping on a baking chamber with an ion pump and a TSP, the photoemission system is brought down to experimental operating pressures in the high $10^{-11}$ torr range.

It should be noted that constant pumping is required to maintain UHV conditions. The interior chamber surfaces will continuously outgas adsorbed molecules, such as water vapor, that are collected from exposure to the atmosphere, and certain scientific techniques, such as sputtering with $\text{Ar}^+$, introduce additional gas molecules into the photoemission system. Over extended periods of time, the dominant need for constant pumping is the diffusion of hydrogen gas through the chamber walls. Although this process is slow, it delineates the minimum bound of attainable vacuum in the low $10^{-11}$ torr range.

While the pressure in a photoemission system can be derived from the ion pump current, as it is proportional to the number of gas molecules being ionized and removed from the system, it is more common to use a Convectron thermocouple gauge or a Bayard-Alpert ion gauge. A thermocouple gauge is effective from pressures of 1000 down to $10^{-4}$ torr and is composed of a heater filament in contact with a thermocouple junction. It determines the vacuum pressure as it relates to the thermal conductivity of the gas in the system. The better thermal insulation inherent to the reduced convection at lower pressures results in higher thermocouple readings. An ion
gauge is effective from pressures of $10^{-4}$ down to $10^{-11}$ torr and uses high energy electrons to ionize gas molecules. These ions are drawn to a collector electrode whose current is proportional to the pressure.

### 2.5.3 Energy Analyzer

Not only does UHV allow photoemission to probe clean sample surfaces, but it also permits the operation of the electron energy analyzers required to perform spectroscopy. The data in this thesis were primarily collected with a Gammasdata Scienta Electron Spectrometer (SES-100), shown in Figure 2.14. Addition data were collected with an Omicron EA-125 electron
spectrometer. Both the SES-100 and the EA-125 are hemispherical analyzers that operate on the same physical principles, with the primary difference being the Scienta’s two-dimensional detector that allows for the simultaneous detection of multiple emission angles and multiple energies. These analyzers permit the selection and detection of emitted photoelectrons possessing particular energies and angular distributions.

As depicted in Figure 2.15, photoelectrons from the sample pass through a series of electric focusing lenses and enter the analyzer through a slit between two hemispheres. The slits can be adjusted to several different width and shape settings, and the hemispheres for the SES-100 have a mean radius of 100 millimeters. The hemispheres $R_1$ and $R_2$ are biased at voltages $\pm V$ and the resultant electric field compels the electrons to travel a hemispherical trajectory until they encounter the detector. While the analyzer electric field ends at a terminating wire mesh, the electrons are incident upon a set of micro-channel plates (MCP) that multiply their number by a factor of
10^6. These electrons encounter a phosphor screen, creating a proportional number of light flashes that are recorded by a charge-coupled device (CCD) camera.

Electron counts are displayed on the two-dimensional Scienta phosphor screen with kinetic energy variations along the vertical axis and CCD channel along the horizontal axis [17]. When used to differentiate electrons in momentum space, the channels are binned into slices that correspond to differences in emission angle. A typical angle-resolved photoemission scan using the SES-100 is presented in Figure 2.16 where, for fifty detector slices, normal emission is around slice 24. The bulk state observed dispersing to lower kinetic energy away from normal emission can be seen to exhibit the polarization-dependent intensity variations discussed in Section 2.2.

If the hemispheres are biased by ±V, the kinetic energy of an electron of charge e travelling along the average central path R_0 is the pass energy

$$E_P = \frac{2Ve}{\frac{R_2}{R_1} - \frac{R_1}{R_2}}. \quad (2.10)$$

The resultant analyzer energy resolution ΔE can be adjusted by altering the pass energy and the entrance slit width d and is to first order

$$\Delta E = E_P \frac{d}{2R_0}. \quad (2.11)$$
From this relationship it can be seen that hemispherical analyzers with larger radii can attain higher energy resolutions. There is a tradeoff in that better energy resolution comes at the expense of photoelectron intensity. Smaller slit width and lower pass energy increase the energy resolution, but they also reduce the total electron counts incident upon the detector. Although the SES-100 can provide a resolution of 1 meV, it is typically operated at an order of magnitude lower resolution to provide a statistically significant number of counts within a reasonably short period of time. Each beamline also has an inherent energy resolution that, at a given photon energy, can be tuned via the entrance and exit slits with a similar intensity tradeoff. The analyzer and beamline resolutions can be added in quadrature to obtain a total energy resolution. In an experiment, the photoelectron yield and energy resolution need to be balanced for practical considerations.

Due to its multichannel capabilities, the Scienta analyzer also has a finite angular resolution for each slice bin. Both the analyzer slit width and the angular mode of the lenses contribute additionally to this resolution. The slit width allows modulation of the angular acceptance, with a larger acceptance decreasing the angular resolution. The angular mode defines the angular range recorded on the phosphor screen with a reduced total range corresponding to an increased resolution, as displayed in Table 2.2. The energy and angular resolution attainable with modern electron energy
Table 2.2: Summary of angular acceptances and resolutions for the Scienta Angular modes. Optimal angular resolution obtained with entrance slit set to 0.2 mm [18].

<table>
<thead>
<tr>
<th>Angular Mode</th>
<th>Angular Range</th>
<th>Optimal Angular Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.73°</td>
<td>0.2°</td>
</tr>
<tr>
<td>2</td>
<td>2.86°</td>
<td>0.1°</td>
</tr>
<tr>
<td>3</td>
<td>1.43°</td>
<td>0.05°</td>
</tr>
</tbody>
</table>

analyzers permits photoemission spectroscopy to probe sample electronic structures with a high degree of accuracy.

2.6 Advantages of Photoemission

Electrons have a number of advantages over photons, atoms, and ions as the probes of choice for surface spectroscopy, through which they have found wide application in the field [5]. To summarize:

1. The small escape depth of electrons make them well-suited to the study of electronic states in the sample surface region.

2. Electrons can be focused and their energy tuned easily via electric fields.

3. The detection and tallying of electrons are easy.

4. Electron energy analyzers with high energy and angle resolution are readily available.

5. Unlike atoms and ions, electrons do not accumulate after they have been detected, nor do they usually alter the sample physically.

These characteristics make photoelectron spectroscopy an excellent tool for studying the electronic structures of thin films and other surface systems.
3 Surface Systems and Thin Films

3.1 Introduction

The particular electronic structure of a crystalline solid derives from the interactions between its electrons and its lattice. The regular arrangement of component atoms creates a dominant periodicity in both real and reciprocal space. Under the influence of the repeated atomic potentials, individual valence electron states transform into an electronic band structure that spans the Brillouin zone. The dispersion of these momentum-dependent electron energy states reflects the symmetries of the crystal lattice and defines the bulk conduction properties of metals and semiconductors [7].

New behaviors manifest when a solid deviates from its ideal bulk crystal, such as at a surface, in a film, or at the interface between two crystals. A terminating plane that breaks the crystal lattice symmetry creates new electronic states and periodicities that are characteristic of the surface. The electrons in a crystal that is limited in extent to a few atomic layers in one or more spatial dimensions, such as a film, wire, or dot, encounter finite boundary conditions that alter their states and can even confine them. Discontinuities at the interfaces between different crystals can lead to the redistribution of strain and charge. These non-bulk environments produce electronic and physical properties that are of interest both from a pure science and an applied technology perspective.

3.2 Crystal Lattices

A crystal is, by definition, a homogenous solid formed by a repeating, three-dimensional pattern of atoms, ions, or molecules having fixed distances between constituent parts. The fundamental configuration of atoms that composes the crystal is the unit cell. These identical units are patterned throughout space to form a periodic lattice, and the bulk condition exists when the lattice boundaries can be considered to extend to infinity. Such an infinite array of discrete points, with an arrangement and orientation that appears exactly the same from whichever of the points the array is viewed,
Figure 3.1: (a) The structure of the fcc lattice. (b) The structure of the diamond lattice, with the displacement vector $\mathbf{R}$ indicating the two atom basis. Adapted from [7].

is termed a Bravais lattice. The lattice periodicity defines the crystal properties both in real and momentum space.

3.2.1 Spatial Lattice

To form the physical lattice of a crystal, its unit cell is repeated via spatial translations along the crystal axes, a set of three non-coplanar vectors that corresponds to the three edges of the unit cell. While the unit cell can be defined in terms of the minimum volume required to tessellate space (the primitive unit cell), it is more commonly described by the conventional unit cell, which possesses an integer multiple volume of the primitive unit cell. The most basic class of conventional unit cells belongs to the cubic lattices, consisting of simple cubic, body-centered cubic, and face-centered cubic. Their crystal axes are composed of three orthogonal vectors ($\mathbf{a}_1 = a\hat{x}$, $\mathbf{a}_2 = a\hat{y}$, and $\mathbf{a}_3 = a\hat{z}$) with identical magnitudes $a$ referred to as the crystal’s lattice constant. Pb, with a lattice constant $a_{\text{Pb}} = 4.95$ Å, has a face-centered cubic (fcc) lattice, as depicted in Figure 3.1(a).

A basis is the configuration of the individual constituents within a unit cell. While the simplest crystals have a single atom basis for each lattice point, more complex crystals can be formed from bases composed of multiple atoms. One of the most common is the diamond structure, shown in Figure 3.1(b), which can be regarded as a face-centered cubic lattice with a two-point basis with one atom at the origin and the other located at the vector position $\mathbf{R} = \frac{1}{4}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$. Given that each atom in the diamond crystal basis is repeated with fcc periodicity, such a crystal can be viewed as a pair of interpenetrating fcc lattices displaced by the vector $\mathbf{R}$. The lattice
constant for a diamond crystal is still defined in terms of the conventional unit cell cube edge. The common semiconductor Si has a diamond structure crystal with lattice constant $a_{Si} = 5.43$ Å.

Directions within a crystal are specified relative to the lattice planes and are expressed via Miller indices. The Miller indices for a particular crystal plane are defined as the set of integers $(h k l)$ with no common factors that are inversely proportional to the intercepts of the plane along the crystal axes. For a crystal plane with orientation $(h k l)$, the direction $[h k l]$ is the normal to the plane. Three common plane orientations for cubic lattices are (100), (110), and (111), as shown in Figure 3.2. Both the single-crystal silicon wafers used as substrates in this work and the Pb overlayers formed on them have a (111)-oriented structure in the growth direction [19,20].

The spacing between crystal planes depends on both the plane orientation and the particular crystal basis. For the simple fcc crystal with lattice constant $a$ in Figure 3.3(a), the cube diagonal spans four evenly-spaced planes and so adjacent (111) planes are separated by $a/\sqrt{3}$. As it pertains to Pb(111) film thicknesses, $a_{Pb}/\sqrt{3}$ (2.86 Å) corresponds to one atomic layer or monolayer (ML), about $9.43\times10^{14}$ atoms/cm². In a diamond structured crystal like Si, successive planes are unevenly spaced along the cube diagonal. This produces a series of bilayers in the (111) orientation, as shown in Figure 3.3(b), with alternate separations of $\sqrt{3}a/12$ and $\sqrt{3}a/4$.

### 3.2.2 Reciprocal Lattice

The electronic structure and scattering properties of a crystal are defined in momentum space (or $k$-space) by its reciprocal lattice, which is the set of all wave vectors that yield plane waves with the periodicity of a crystal’s Bravais lattice. The reciprocal lattice is itself a Bravais lattice and the transformation between direct and momentum space is reflexive for cubic
Figure 3.3: (a) The (111) planes of the fcc lattice. (b) The (111) planes of the diamond lattice form three sets of bilayers per unit cell with the interlayer spacings shown.

lattices. Simple cubic real space lattices correspond to simple cubic reciprocal lattices and real fcc lattices, such as Pb, transform to body-centered cubic lattices in k-space. The primitive unit cell about a reciprocal lattice point composed of the region of k-space that is closer to that point than to any other lattice point is termed the first Brillouin zone. A real space fcc crystal has the bulk Brillouin zone pictured in Figure 3.4, with its high symmetry points and directions labelled by letters. For example, movement through reciprocal space from the zone center, Γ, along the [111] direction, Λ, terminates on the zone boundary at L.

If a trajectory is followed through reciprocal space far enough, it will cross the boundary from the first Brillouin zone into the second and then into successively higher-order zones. The periodic nature of the lattice manifests itself in properties such as the crystal electronic structure, as it derives from the interaction between the individual atomic electron wave functions and the lattice potential. The electron band structures for Pb and Si are presented in Figure 3.5. Each diagram plots the electron energy levels as
a function of wave vector as $k$-space is traversed along the high symmetry directions of the crystal Brillouin zone. Electrons fill the energy bands up to the Fermi level and the position of $E_F$ relative to the band structure determines the conduction properties of the material. If a band crosses the Fermi level, as in the Pb structure, then the material is a metal, but if the Fermi level lies within a relatively narrow band gap, as in Si, the material is a semiconductor.

### 3.3 Crystal Surfaces

In any real system, a crystal does not extend to infinity but rather possesses a surface. The planar termination of a lattice introduces a finite boundary condition that breaks the translational symmetry of the crystal. This deviation from ideality results in surface properties, both in real and reciprocal space, that differ from the bulk condition.

#### 3.3.1 Real Space

The surface of a crystal depends on the particular plane that terminates the bulk lattice. Figure 3.6 compares the (001) and (111) $fcc$ surfaces, and it
can be seen that the $1 \times 1$ cell varies with the plane orientation. These low-index planes produce surfaces characterized by rotational symmetry. The identical nature of the $[100]$ and $[010]$ directions creates a four-fold symmetry on the (001) surface. Similarly, when considering only its top layer, the (111) surface exhibits six-fold symmetry, as the set of $\langle 2 \bar{1} \bar{1} \rangle$ directions repeats at $60^\circ$ intervals with the $\langle 110 \rangle$ directions offset by $30^\circ$. When lower layers are considered, however, both fcc and diamond lattice surfaces only exhibit three-fold rotational symmetry. Commercial Si(111) wafers are standardized to have their primary flat oriented parallel to one of the $\langle 2 \bar{1} \bar{1} \rangle$ directions.

**Figure 3.5:** Band structures for Pb and Si. The Fermi level is marked by a dashed line.
The bulk termination of a crystal surface often produces an arrangement of atoms and bonds that is not energetically optimal. Driven by energy minimization, the surface atoms can configure into a stabilized reconstruction that is characterized by a two-dimensional periodicity. The reconstruction is usually expressed in coordinates related to the periodicity of the underlying bulk-terminated plane, specifically in reference to the 1×1 unit surface unit cell. A reconstruction denoted by \( n \times m \) \( R\theta \) has a periodicity of \( n \) bulk units by \( m \) bulk units, rotated by \( \theta \) degrees relative to the surface 1×1 unit cell. Figure 3.6 displays typical reconstruction periodicities on the (001) and (111) \( fcc \) surfaces.

One common reconstruction is the Si(111)-7×7 surface. This complex yet well-characterized structure pacifies the dangling bonds of the bulk-terminated plane through a series of dimers, adatoms, and stacking faults [21]. It is obtained by resistively heating a commercial Si(111) wafer to roughly 1250° C for 7 to 10 seconds. This process, called flashing, removes the surface oxide layer and provides the requisite thermal energy for the silicon atoms to rearrange into the 7×7 ordering. The preparation of all the samples in this work begins with the clean Si(111)-7×7 surface as a substrate.

The addition of heterogenous atoms to a surface can also lead to the formation of a reconstruction. This is accomplished in this thesis by depositing a small amount of a metal (Au, Ag, In, or Pb) on the clean Si(111) surface, followed by annealing [22-25]. The process eliminates the 7×7 substrate structure and allows the deposited metal atoms to reorder the surface into
Reconstruction Coverage [ML] Reconstruction Coverage [ML]

<table>
<thead>
<tr>
<th>Au-5×2</th>
<th>0.42</th>
<th>Ag-(\sqrt{3} \times \sqrt{3})</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-(\sqrt{3} \times \sqrt{3})-α</td>
<td>0.76</td>
<td>In-(\sqrt{3} \times \sqrt{3})</td>
<td>0.33</td>
</tr>
<tr>
<td>Au-(\sqrt{3} \times \sqrt{3})-β</td>
<td>0.96</td>
<td>Pb-(\sqrt{3} \times \sqrt{3})-β</td>
<td>0.33</td>
</tr>
<tr>
<td>Au-6×6</td>
<td>0.96</td>
<td>Pb-(\sqrt{3} \times \sqrt{3})-α</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Table 3.1: Various metal reconstructions on Si(111).

a new periodicity. As it applies to deposition on a substrate, one monolayer is defined in terms of the number of surface sites, which for Si(111) is \(7.83 \times 10^{14}\) atoms/cm\(^2\). The particular reconstruction formed depends on the type and quantity of metal deposited and the annealing conditions. Table 3.1 summarizes the reconstructions formed on the Si(111) surface by different concentrations of various metals. These reconstructions are created by annealing the system to between 300 and 600°C, usually followed by a quench. Although the Au-6×6 and Au-\(\sqrt{3} \times \sqrt{3}\) structures have the same metal coverage, they differ in that the Au-6×6 arrangement forms through a slow post-anneal cool down. In most cases, the metal atoms sit on top of a full bilayer of the Si(111) surface. One notable exception to this configuration is the Ag-\(\sqrt{3} \times \sqrt{3}\) reconstruction in which the Ag atoms reside on a single-layered Si(111) plane. All of these metal-terminated Si(111) surfaces are stable at room temperature and below, and their long range lateral periodicities provide well-ordered surfaces useful for further work.

### 3.3.2 Reciprocal Space

The interruption of a crystal lattice by finite boundary conditions also alters its reciprocal lattice and the related electronic structure. The termination produces a two-dimensional surface Brillouin zone (SBZ), as shown for the (111) face of the fcc lattice in Figure 3.7. This SBZ is a hexagon with the zone center denoted by \(\bar{\Gamma}\), the zone boundary corner by \(\bar{K}\), and the zone boundary edge medians by \(\bar{M}\) and \(\bar{M}'\). The bulk \(k\)-space direction \(\Gamma L\), which is perpendicular to the crystal surface as it runs collinear with \([111]\), terminates at \(\bar{\Gamma}\). For the Si(111) surface, \(\bar{\Gamma} \bar{K}\) is parallel to \(\langle 110 \rangle\) and \(\bar{\Gamma} \bar{M}/\bar{M}'\) is parallel to \(\langle 211 \rangle\).

The surface Brillouin zone is the region in \(k\)-space primarily probed by photoemission. Normal emission corresponds to the zone center \(\bar{\Gamma}\). By varying \(k_\parallel\), the surface electronic structure can be scanned from \(\bar{\Gamma}\) out toward the SBZ boundary. This is accomplished by rotating the sample relative to the analyzer in order to record electron emission at different values of \(\theta\) and \(k_\parallel\). Usually the sample is oriented such that \(k_\parallel\) moves along either the \(\bar{\Gamma} \bar{K}\) or
Figure 3.7: The fcc(111) surface Brillouin zone [26].

The bulk Brillouin zone is scanned along $\Gamma L$ by varying the photon energy. Through this process the entire energy band structure of the system can be mapped. States arising from reconstructions or other surface effects often appear in the bulk band gap, which in the photoemission spectrum for Si(111) lies between the top valence band and the Fermi level.

3.3.3 Surface Preparation and Characterization

Molecular beam epitaxy (MBE) is a standard technique for depositing a material onto a substrate in UHV. In this process, the desired depositant is heated at a controlled temperature to create a beam of atoms by either sublimation or evaporation. The substrate is positioned in the path of the beam such that the atoms can impinge and adsorb. The evaporation rate depends directly on the heating conditions, which gives MBE a high degree of precision control over the growth behavior. This control makes MBE well suited to surface reconstruction and thin film growth.

A schematic diagram of the MBE apparatus used in this work is depicted in Figure 3.8. The substance to be evaporated is placed in a crucible made from an inert material with a high melting point, such as Mo, W, or Ta, which is positively biased with high voltage ($+0.5-2.0$ kV). Current passing through a separate tungsten filament produces electrons through thermionic emission that are accelerated toward the biased crucible. When the electrons strike the crucible, their kinetic energy transforms to heat, increasing the temperature of the target material. The crucible temperature, and thus the evaporation rate, depends on two parameters: the filament emission current, which corresponds to the number of electrons striking the crucible, and the
crucible voltage, which determines the kinetic energy of the electrons. In this apparatus, the filament current is controlled by a feedback system that maintains a constant emission current and a steady evaporation rate. For the evaporator used in this work, Pb typically evaporates at a rate of 1 ML per minute when the filament emission current is set to 5 mA and the crucible voltage to 0.5 kV.

A crystal thickness monitor (XTM) placed in the beam path near the substrate location is used to measure and calibrate the evaporation rate. The frequency of a quartz crystal’s oscillations is monitored during deposition. As material adheres to the XTM surface, the vibration frequency changes in a process analogous to the addition of mass to an oscillatory spring system. The amount of material deposited over a period of time can be determined

Figure 3.8: Schematic representation of the molecular beam epitaxy apparatus [27].
Table 3.2: Conversion factors $C$ from Å to ML for various metals on Si(111) surface, where $[\text{ML}] = C[\text{Å}]$. The surface factor applies to low-coverage depositions (used in the formation of reconstructions) for which the substrate site density defines a monolayer. The film factor applies to higher-coverage depositions (used in the growth of films) for which the spacing between crystal $fcc(111)$ planes is relevant.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Surface</th>
<th>Film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.748</td>
<td>0.424</td>
</tr>
<tr>
<td>Au</td>
<td>0.753</td>
<td>0.424</td>
</tr>
<tr>
<td>In</td>
<td>0.489</td>
<td>0.480</td>
</tr>
<tr>
<td>Pb</td>
<td>0.423</td>
<td>0.350</td>
</tr>
</tbody>
</table>

From the frequency change. The XTM expresses this amount in thickness units of Angstroms, which can be converted to monolayers as defined in Sections 3.2.1 and 3.3.1. When considering surface coverages, the conversion factor depends on both the substrate and the adsorbed material and is given by

$$
\Theta = \frac{NA \rho}{W_M \delta_S} t, \tag{3.1}
$$

where $\Theta$ is the thickness in monolayers, $t$ is the thickness in Å, $N_A$ is Avogadro’s number, $\rho$ and $W_M$ are the density and molecular weight of the evaporant, respectively, and $\delta_S$ is the site density of the substrate surface. Table 3.2 presents a compilation of thickness conversions for several metals on Si(111).

Electron diffraction is the primary tool for characterizing the sample surface to ensure that it is well-ordered. This work employs the technique of reflection high-energy electron diffraction (RHEED) to probe the surface periodicity. As shown in Figure 3.9, a high-energy beam of electrons strikes the sample surface at a grazing angle. This small incidence angle, about $3^\circ$, ensures that the electron penetration depth is limited to the first few layers of the surface and thus RHEED is surface sensitive. The electrons are both reflected and diffracted by the surface, after which they illuminate a fluorescent screen. The diffraction pattern observable on the screen correlates to the surface periodicity. The geometry employed in RHEED allows it to be used simultaneously with MBE to monitor the changes in surface periodicity during deposition.

By rotating the sample around the surface normal, the electrons can diffract along the surface’s high-symmetry directions. When this occurs, the pattern appears as a set of centered rings composed of diffraction spots, as shown in Figure 3.10. This representative RHEED pattern was formed by an electron beam energy of 10 keV, and it comes from the Si(111)-7×7...
surface. Spots originating from bulk lattice diffraction can be differentiated from surface diffraction spots due to their greater dependence on sample orientation, as the bulk diffraction condition is constrained in three, not two, dimensions. The $n \times n$ surface periodicity can be deciphered from the pattern because there are $n - 1$ rings between each primary ring, each with $n - 1$ spots between each 1×1 spot. RHEED patterns that exhibit small, well-defined diffraction spots of a single periodicity with a low background are indicative of a high quality surface.

3.3.4 Film Growth

The Pb films employed in this thesis research were prepared through the following procedure. The Si(111) substrates were cut from commercial $n$-doped wafers with a resistivity of 1-60 Ω-cm. The Si(111)-7×7 surface was formed via flashing. An appropriate amount of the terminating metal was deposited onto the clean Si(111) surface by MBE and followed by annealing to form one of the reconstructions in Table 3.1. Both the clean and reconstructed Si(111) surfaces were characterized with a combination of RHEED and valence band spectroscopy to ensure high quality. Thin Pb films were then grown over the substrates with MBE at either 60 or 100 K. The low substrate temperature during deposition was essential for forming smooth films. The resulting films were normally oriented along the (111) direction,
exhibiting parallel epitaxy and a large lattice mismatch relative to the substrate.

### 3.4 Quantum Well States

Material deposited on to a surface can aggregate in a multitude of manners. While reconstructions with the substrate sometimes form at sub-monolayer coverages, larger deposition quantities display one of three growth modes [19, 20]. The layer-by-layer, or Frank-van der Merwe (FM), growth mode occurs when atoms of the deposited material are more strongly attracted to the substrate than they are to themselves. The opposite case, Volmer-Weber growth (VW), in which the atoms are strongly bound to each other, leads to the formation of islands. An intermediate case, the Stranski-Krastanov mode (SK), arises when the initial formation of a wetting layer is subsequently followed by island growth. The deposited material can develop into a film through layering or island coalescence. A film is characterized by the wide lateral proportion of its crystal structure relative to its thickness. Like other configurations of limited spatial extension such as dots and wires,
the electronic structure of a film can differ substantially from that of its bulk crystal.

3.4.1 Electron Confinement and Quantization

The electrons within an ideal free-standing film are confined within the film by the surrounding vacuum. In reality, films are grown on substrates, so when electron states within the film overlap with states in the substrate, no confinement will occur. Conversely, if the film electrons fall within a gap in the substrate band structure, then the electrons will remain confined in the overlayer. Confinement can arise in a metal-on-metal system when the substrate band structure exhibits a relative gap in comparison to the film, as in the Ag/Fe(001) system [29–31]. For a metal-on-semiconductor system such as Pb/Si(111), the metal electrons are confined by the semiconductor band gap [25,32,33]. For this particular system, the relevant direction in real space is the [111] direction, which is the surface normal for both the substrate and the film and which corresponds to the ΓL direction in k-space. A comparison of the two band structures in Figure 3.11 shows that electrons with energies near the Fermi level in Pb have no corresponding states in Si above the valence band maximum (VBM) to which they can transition and thus they are confined in the film.

Electrons confined between the vacuum and the film-substrate interface potential barriers exist in “particle in a box”-type states called quantum well states (QWS) [34–37]. The electron states are only quantized in the direction perpendicular to the film, as the lateral expanse of the film is not restricted. Quantum well states are characterized by energies that change discretely at integer film monolayer thicknesses. Quantum well states, as presented in Figure 3.12, appear in photoemission spectra as sharp, intense peaks in the confinement range between the top of the substrate band maximum and the Fermi level. States arising from electrons with energies outside the confinement range but whose wave functions are partially confined are termed quantum well resonances, and they appear as less intense, broader peaks at higher binding energies in photoemission spectra. When the film thickness changes, the energies of the quantum well peaks shift discontinuously.

3.4.2 The Bohr-Sommerfeld Phase Model

As a confined electron traverses a film, its wave function accumulates a phase shift not only in transit, but also when it is reflected from the vacuum and substrate interfaces. The total phase shift must sum to an integer multiple
of $2\pi$ to be physical. The quantum well state energy levels are determined by the Bohr-Sommerfeld quantization rule \cite{35–37}:

$$2k(E)Nt + \phi_s + \phi_i = 2n\pi, \quad (3.2)$$

where $k$ is the electron momentum, $E$ is the energy of the state, $N$ is the number of monolayers, $t$ is the monolayer thickness, $\phi_s$ and $\phi_i$ are the energy-dependent phase shifts at the surface and interface, respectively, and $n$ is a quantum number. Both $k(E)$ and $\phi_s(E)$ are typically known from first principle calculations while $\phi_i(E)$ can be described by several phenomenological models. The Bohr-Sommerfeld equation defines an electron energy value for each set of integers $N$ and $n$.

Figure 3.13 shows the theoretical spectrum of quantum well state energies at the SBZ center (normal emission) for a free-standing Pb film over a range of thicknesses \cite{38}. Both faces of the film border the vacuum and so $\phi_i = \phi_s$. A change in thickness of only one atomic layer noticeably alters the electronic structure. At low thicknesses, the electron energies are spaced relatively far apart but their separation decreases at higher coverages. The quantized nature of the electronic structure is therefore readily apparent for thin films, but the energy states appear continuous as the film becomes
increasingly bulk-like.

The electronic quantization perpendicular to the film divides each of the bulk bands into a set of subbands. A film composed of \( N \) monolayers will have its valence bands split into \( N \) subbands. The subband dispersion is primarily determined from the unquantized bulk band structure, although interface effects arising from the substrate band structure can also contribute \([33,39]\). Typically, only the portions of subbands with energies in the confinement range are apparent in photoemission spectra. Figure 3.14 shows the subband dispersion in the \( \bar{\Gamma} \bar{K} \) direction for a 6 ML-thick Pb film grown on the Ag-\( \sqrt{3} \times \sqrt{3} / \text{Si(111)} \) surface. As expected for a free-electron-like metal, the Pb quantum well states disperse parabolically in the \( k \)-space range immediately around the zone center (but not at larger \( k_{||} \)).

### 3.4.3 Atomic Layer Resolution

As seen in Figures 3.12 and 3.13, the quantum electronic structure of a thin film is sensitive to changes in thicknesses as small as one atomic layer. This characteristic can be used to monitor the roughness of the film surface and to determine its thickness with monolayer accuracy \([32]\). Quantum well peaks in photoemission spectra reach their maximum intensity when they are fully developed at integer monolayer film thicknesses. By monitoring the peak intensities as a function of deposition time, the interval between suc-
cessive monolayers can be measured. Subsequent extrapolation permits the determination of the absolute film thickness. This layer counting method is used to calibrate the film thicknesses for the thin films grown in this thesis. Figure 3.15 shows plots of quantum well peak intensity as a function of deposition time for Pb films grown on the Au-6×6/Si(111), In-√3×√3/Si(111), and Ag-√3×√3/Si(111) surfaces.

Since every integer film thickness supports a different quantum well peak, the photoemission spectrum for a film composed of several thicknesses will display multiple peaks. The numerous peaks exhibited by a rough film can preclude the atomic layer resolution required to perform a layer counting thickness calibration. Conversely, a perfectly smooth film’s spectrum will not show quantum well peaks for any thickness other than its exact coverage. This quality has permitted the identification of atomic uniformity for the Ag/Fe(001) and Pb/Si(111) systems in Figure 3.12 [25, 29]. In general, atomic layer resolution and absolute film thickness calibration is necessary for the analysis of quantum well states.

**Figure 3.13:** Calculated QWS energies for a free-standing Pb film [38]. The dashed line connects states of the same quantum number $n$. 
Figure 3.14: Photoemission intensity for a Pb film of thickness 6 ML grown on the Ag-$\sqrt{3} \times \sqrt{3}$/Si(111) surface as a function of energy and parallel wavevector $k_{||}$ in the $\Gamma K$ direction. The solid curves are the subband dispersions arising from the Pb valence band as calculated with the Naval Research Laboratory’s static tight-binding program.

3.5 The Schottky Barrier

The electronic structure that arises when a metal film is grown on a semiconductor substrate is characterized by the Schottky barrier. The Schottky barrier is the rectifying energy barrier for electrical conduction across a metal-semiconductor junction and it is critical to solid-state device design as it defines the transport behavior across the metal-semiconductor interface [40–60]. The height of the Schottky barrier reflects the mismatch in the energy position of the majority carrier band edge of the semiconductor and the metal Fermi level at the interface. For a metal film on a $p$-type semiconductor, the barrier height is the difference between the valence band maximum and the Fermi level. If the semiconductor is $n$-type, the Schottky barrier height is the difference between the conduction band minimum of the semiconductor and the metal Fermi level. As shown in Figure 3.16, the Schottky barrier height is also the difference between the semiconductor band gap and the confinement region for the latter system, and thus is directly coupled to the film’s quantum well electronic structure. Although the phenomenological properties of the Schottky barrier are well understood, its origin has been question of long-standing interest.
Figure 3.15: Quantum well peak intensities measured as a function of Pb deposition time for films grown on the Au-6×6/Si(111), In-$\sqrt{3} \times \sqrt{3}$/Si(111), and Ag-$\sqrt{3} \times \sqrt{3}$/Si(111) surfaces. The average interval between successive peak maxima is correlated to monolayer spacing, thus determining an absolute film thickness calibration.

3.5.1 Measuring the Schottky Barrier

While several methods can be employed to determine the height of the Schottky barrier, most measurements have relied on core level photoemission spectroscopy. The binding energies of the substrate core level peaks are monitored as a metal is deposited on a clean semiconductor. The peak shifts are correlated to the position of the semiconductor VBM relative to
Figure 3.16: Schematic representation of the metal-semiconductor interface electronic structure for an n-type semiconductor. The Schottky barrier height is the difference between the semiconductor band gap $E_g$ and the confinement range $E_0$. The Fermi level, providing a measure of the barrier height. This method is generally limited to a few atomic layers of metal for which the interface and the overlayer are not necessarily fully developed, thus it is difficult to separate out effects pertaining to the surface, the adsorbate, and the interface. Photovoltaic effects have also been shown to obscure the accurate measurement of barrier heights in core level studies of ultrathin films [55].

Diode measurements of the barrier height are free from such uncertainties, as $I-V$ readings are taken directly across metal-semiconductor junctions connected in circuit with an Ohmic contact on the semiconductor and a gold contact on the metal. Statistically significant diode measurements require averaging over a set of mass-produced samples, however, and the presence of macroscopic contacts can obscure effects that arise from atomic-level fluctuations. Epitaxial sample fabrication of single-crystal films with atomically controlled interfaces is extremely difficult, and existing data are scarce [57,59].

Given the interrelation of the Schottky barrier, the confinement range, and quantum well energies, the barrier height should also be directly determinable through an evaluation of the quantum well peaks in valence band photoemission spectra [46]. The simultaneous measurement of the valence band maximum and the Fermi level eliminate the problems inherent to core
level analysis and the spectroscopic methodology ensures atomic-level sample quality that is unattainable in diode measurements. Previous experiments have deduced the Schottky barrier height by estimating the position of the VBM from quantum well peak positions [18]. A more rigorous method, based on the quantitative evaluation of quantum well energies as functions of film thickness, is developed in Chapter 4.

3.5.2 Modelling the Schottky Barrier

The earliest formulation of the Schottky barrier’s origin, the Schottky-Mott model, depended solely on the bulk characteristics of the metal and semiconductor [40]. It gave the barrier height $S$ as:

$$S = \phi_M - \chi_S$$

(3.3)

where $\phi_M$ and $\chi_S$ are the metal work function and the semiconductor electron affinity, respectively. Experimental measurements of the barrier height failed to display the strong dependence on the metal work function dictated by the Schottky-Mott model. In contrast, the barrier heights for numerous polycrystalline metal-semiconductor systems were observed to be insensitive to the particular metal in a phenomenon termed Fermi-level pinning. Several models developed to account for these results postulated mechanisms such as surface and gap states that would make the barrier height insensitive to the metal work function [40]. The subsequent fabrication and Schottky barrier height measurement of several high-quality epitaxial metal-semiconductor systems revealed a rather dramatic dependence on the structure of the interface [56–60]. For example, the Schottky barrier height for a Pb film grown on the Pb-√3 × √3/Si(111) surface was observed to be 74 meV greater than that for the same film grown on the Si(111)-7×7 surface [59]. The experimental verification of the Schottky barrier’s interface dependence has given credence to the current barrier theories built around bond polarization. In these models, such as that proposed in Chapter 4, the Schottky barrier height depends on the interfacial bonding specifics as well as the bulk properties of the metal and the semiconductor.

3.6 Thermal Stability

The thermal stability temperature of a film is the threshold annealing temperature at which the film’s structure begins to roughen [25, 61]. Above this temperature, the thermal energy provided by heating permits the film
atoms to overcome adsorbate-adsorbate and adsorbate-substrate interaction potentials and transition to a lower energy configuration that is stable at a higher temperature. This process is similar to that undergone by deposited metals being annealed to form a surface reconstruction. While the functional properties of a macroscopic film are insensitive to atomic fluctuations, the electronic and physical properties of nanoscale films can be altered dramatically if the film thickness changes by a single monolayer. An ultrathin film must remain structurally robust under operating conditions to be useful in technological applications. Its thermal stability temperature determines the maximum temperature at which it remains smooth and functional.

Certain film thicknesses will be more stable than others. For example, in the prototypical metal-on-metal system of Ag films grown on Fe(001), films with thicknesses of $N = 1, 2,$ and $5\text{ ML}$ have stability temperatures in excess of 800 K while all other thickness films have stability temperatures around 300-400 K [61]. This thickness-dependent stability behavior is depicted in Figure 3.17. The thermal stability, the total electronic energy, and the electronic subband structure of an atomically uniform thin film are all interrelated. As seen in Section 3.4, the quantized subbands depend on the number of monolayers composing the film. The electronic structure subsequently determines the electronic energy of the film. There can be significant layer-to-layer variation in the total film electronic energy because the electronic states are quantized. The film’s energetic stability is defined by the second derivative of the total electronic energy with respect to the film thickness and is related to the thermal stability temperature. A film of a given number of atomic layers is locally stable when it is energetically unfavorable for its atoms to rearrange into films of adjacent thicknesses. The two calculations for the second derivative of film energy for the Ag/Fe(001) system as a function of thickness in Figure 3.17 display large positive values for $N = 2$ and $5$, indicating that they are electronically more stable than other numbers of layers.

This electronic stabilization also causes the formation of plateaus with preferred “magic thickness” heights observed in some metal-semiconductor systems and it is similar to the stabilization of nanoclusters and nanowires by closed electronic shell configurations. Given the intertwined natures of thermal stability and electronic structure, the thickness dependence of the film stability temperature can be probed with quantum well spectroscopy. The analysis presented in Chapter 5 elucidates the relationship between the film electronic structure and its thermal stability for the Pb/Si(111) system.

46
Figure 3.17: (a) Thermal stability temperatures of Ag films grown on Fe(001) measured via photoemission. The $N = 5$ ML film is stable up to the highest temperature used in the experiment and the arrow indicates that the data point represents a lower bound. (b) and (c) Calculated second derivatives of the total film electronic energy with respect to thickness [61].
4 Schottky Barrier Tuning

4.1 Overview

The physical phenomenon of the Schottky barrier at a metal-semiconductor junction was first reported over sixty years ago but its origins are still not well understood, in part due to the difficulty inherent to probing a buried interface [40]. As discussed in Chapter 3, this obscurity has not prevented the Schottky barrier’s rectifying property from being incorporated into technological applications. Not only is the determination of the physical mechanism that gives rise to the Schottky barrier an objective of pure scientific interest, but obtaining control over the barrier height would have utility in the field of solid-state electronics.

If electrons are confined in a thin metal film grown on a semiconductor substrate, the interface dependence of the system’s quantum well states can be exploited to study its Schottky barrier. Specifically, a comparison of Pb films prepared on Si(111) surfaces terminated by various metals, called interfactants, allows for the identification of the interfacial contribution to the barrier height. Quantum well spectroscopy is used to determine the barrier height in each case. An analysis of the results establishes that the electronegativity of the metal used for Si termination determines a charge transfer at the interface, which in turn gives rise to an interface dipole layer that determines the barrier height. Schottky barrier heights are predicted based on the standard Mulliken electronegativity table, with no adjustable parameters, and the results are in excellent agreement with the measurements. These findings offer an important insight into the basic atomic-level physics of the Schottky barrier that is important for nanoscale electronic engineering [62].

4.2 The Interfactant Layer

In this study, the Si(111) surfaces were reconstructed with various metals prior to the growth of the Pb films. The material present between the film and the substrate serves as an interfactant layer. By holding the overlayer
and substrate constant while varying the interfactant layer, the effect of the interface on the quantum well electronic structure and on the Schottky barrier height was isolated. A schematic representation of this systematic arrangement is depicted in Figure 4.1.

The metals used for termination include Ag, In, Au, and Pb, and were deposited onto the clean $n$-type Si(111)-7×7 surface by molecular beam epitaxy to form the reconstructions listed in Table 3.1. Reconstructions with well-defined periodicities were chosen because they provide the ordered surfaces necessary to grow smooth films that can support quantum well states. Additionally, the interfactant atoms remain at the interface and do not intermix with the films during Pb deposition [19,63].

Thin Pb films were subsequently grown over the reconstructed substrates at 60-100 K. The resulting films were oriented along the (111) direction and had the same epitaxial structure; thus, the resulting differences can be unequivocally attributed to interfacial effects. The film lattice constant was bulk-Pb-like and incommensurate with the Si substrate lattice, eliminating potential lattice mismatch strain effects. Furthermore, as it is essential that the absolute film thickness be controlled with monolayer precision to employ quantum well spectroscopy, all systems in this study were chosen to meet this requirement. Quantum well data for Pb films grown on the Pb-$\sqrt{3} \times \sqrt{3}$ terminated Si(111) surface were adapted from previous work [25].

Figure 4.1: Schematic representation of an interfactant layer at the junction between a Pb film and a Si substrate.
4.3 Quantum Well Spectroscopy

4.3.1 Energy Level Analysis

An analysis of the photoemission spectra determines the thickness-dependent quantum well energies for each interfactant system. A measurement of the Schottky barrier height can be extracted by fitting these results to a model based on the fundamental quantum mechanics that govern the behavior of confined electrons. These photoemission measurements were performed using 22 eV photons, with the sample at 100 K.

The grey-scale image in Figure 4.2 shows the normal-emission intensity as a function of energy and Pb film thickness for the Au-6×6 terminated Si(111) surface for coverages from 0 to 13 ML. The most notable features are the discrete peaks that represent the confinement of Pb valence electrons between the vacuum and the Si band gap. These peaks are fully developed at integer monolayer film thicknesses, and the atomic layer resolution permits a determination of the absolute film thickness by atomic layer counting [29]. The less intense, broader peaks at higher binding energies are the quantum well resonances derived from partially confined electrons. Similar results for the Pb films grown on the Ag-√3 × √3, In-√3 × √3, and Pb-√3 × √3 terminated Si(111) surfaces are shown in Figures 4.3, 4.4, and 4.5, respectively. Figure 4.6 displays plots of the measured quantum well energy levels for films grown on the set of Au/Si(111) reconstructions studied - 6×6, √3 × √3-β, √3 × √3-α, and 5×2, which have Au coverages of 0.96, 0.96, 0.76, and 0.42 ML, respectively [24]. Figure 4.6 also includes the Pb-√3 × √3 system as a reference for 0 ML Au coverage. The energy levels at a given thickness for the different systems can vary by up to ~1 eV. As described in Equation 3.2, the quantum well energy levels are determined by the Bohr-Sommerfeld quantization rule [35–37]:

\[ 2k(E)Nt + \phi_s + \phi_i = 2n\pi \]  

(4.1)

where \( k \) is the electron momentum, \( E \) is the energy of the state, \( N \) is the number of Pb monolayers, \( t \) is the monolayer thickness, \( \phi_s \) and \( \phi_i \) are the energy-dependent phase shifts at the vacuum surface and substrate interface, respectively, and \( n \) is a quantum number. The substrate interface phase shift \( \phi_i \) has a singularity at the valence band maximum of Si at \( E_0 \) and is given, to the leading order, by

\[ \phi_i(E) = A + B\sqrt{E - E_0} \Theta(E - E_0) \]  

(4.2)
Figure 4.2: (a) Photoemission intensity as a function of energy and film thickness for Pb films deposited on the Au-6×6 terminated Si(111) surface. The intensity maxima (brighter regions) correspond to quantum well states. (b) The solid curves indicated the evolution of the quantum well energies based on a simultaneous fit to the data for the systems. The quantum number \( n \) for each branch is indicated. The dashed lines indicate the branches based on the alternate quantum number \( p = N - 2n - 1 \) used previously for rough films.

where \( A \) and \( B \) are constants and \( \Theta(\cdot) \) is a step function [64]. The bulk band dispersion \( k(E) \) and the vacuum phase shift \( \phi_s(E) \) are known from a first-principles calculation [38]. Equations 4.1 and 4.2 are used to fit the observed quantum well energy levels for the systems simultaneously. The
quantity $B$ is tied to the Si band edge, and should be the same for all systems. The quantity $A$ depends on the atomic details of the interface, and is allowed to vary among the systems. The quantity $E_0$, the confinement energy relative to the Fermi edge, also depends on the system. The Si gap, 1.15 eV, subtracted by $E_0$, equals the Schottky barrier height for the $n$-type substrates [46]. No other fitting parameters are involved. The results of the fit are shown as the solid curves in Figure 4.2 for the Au-6×6 system, and the quantum number $n$ for each branch is indicated. The corresponding fits for the other systems are plotted in Figures 4.3-4.6. The dashed lines

Figure 4.3: Photoemission intensity as a function of energy and film thickness for Pb films deposited on the Ag-$\sqrt{3} \times \sqrt{3}$ terminated Si(111) surface. The same notation conventions as in Figure 4.2 are applied.
represent branches based on the alternate quantum number $p = N - 2n - 1$ in use in the literature [65]. In earlier studies, the films had a significant roughness, causing the peaks as seen in the figures to smear out to form continuous bands following the dashed lines.

### 4.3.2 Peak Width Analysis

An independent determination of the Schottky barrier heights is provided by a measurement of the quantum well peak widths. The results are shown
Figure 4.5: Photoemission intensity as a function of energy and film thickness for Pb films deposited on the Pb-$\sqrt{3} \times \sqrt{3}$ terminated Si(111) surface [25]. The same notation conventions as in Figure 4.2 are applied.

in Figure 4.7, where the circles represent the measured widths for various thicknesses and quantum numbers for the systems. In each case, the measured width exhibits a threshold in energy below which it increases rapidly. States in the quantum well fully confined by the barrier have narrow line shapes, while resonance states with energies outside the barrier are much broader due to degenerate coupling of the electronic states. A substantial change in line width indicates the location of the confinement edge and the barrier height. The vertical lines indicate the midpoint locations bracketed by a sudden change in peak width, and these are seen to well represent the threshold positions. The Schottky barrier heights $S_{\text{expt}}$ synthesized as weighted averages from these measurements and the results of the preceding fit are given in the last column of Table 4.1.
Figure 4.6: Measured (triangles) and fitted (circles) quantum well energy levels for Pb films grown on the Au-$6\times6$, Au-$\sqrt{3}\times\sqrt{3}$-$\beta$, Au-$\sqrt{3}\times\sqrt{3}$-$\alpha$, Au-$5\times2$, and Pb-$\sqrt{3}\times\sqrt{3}$ reconstructed Si(111) surfaces.
Figure 4.7: Width of quantum well peaks as a function of energy for the Pb-$\sqrt{3} \times \sqrt{3}$, In-$\sqrt{3} \times \sqrt{3}$, Ag-$\sqrt{3} \times \sqrt{3}$, Au-5×2, Au-$\sqrt{3} \times \sqrt{3}$-$\alpha$, Au-$\sqrt{3} \times \sqrt{3}$-$\beta$, and Au-6×6 terminations. The vertical line in each case denotes the position of the confinement edge as the midpoint between the adjacent confined and resonant peak widths.
4.4 The Interface Dipole Model

4.4.1 General Two-Parameter Model

The variation in Schottky barrier heights observed for Pb film systems that differ only in interfactant must arise from the disparate conditions at the film-substrate interface. As depicted in Figure 4.8, in the absence of an interfactant each surface Si atom bonds to a film atom. The charge rearrangement along these metal-semiconductor bonds produces a net interface dipole and a resultant potential barrier that contributes to the Schottky barrier height. The presence of an interfactant has the effect of substituting interfactant metal atoms for some proportion of Pb atoms. This effect alters the interface dipole and thus shifts the Schottky barrier height.

Table 4.1 contains the Mulliken electronegativity $\chi$ and the coverage $C$ for the metals at the interface for the metal terminations studied (Ag, In, Au, and Pb) as well as for three other hypothetical cases (Fr, Si, and F) for reference purposes, organized in ascending orders of the electronegativity. The two elements Fr and F represent the two extreme cases on the electronegativity scale of the periodic table. The quantity $Q$ is the average charge state of the Si in direct contact with the interfacial metal ($M$) layer. It is deduced by first evaluating the coverage-weighted electronegativity for the interfacial metal layer (which may be partly Pb), subtracting the electronegativity of Si, and then normalizing the results to one half of the electronegativity difference between F and Fr. Thus,

$$Q = \frac{\left[ C\chi_M + (1 - C)\chi_{Pb} \right] - \chi_{Si}}{(\chi_F - \chi_{Fr})/2}. \quad (4.3)$$

For the hypothetical case of F termination, the numerical result is $Q = 1$. This is the most electronegative element in the periodic table, and the Si in direct contact with F is in the +1 oxidation state. Likewise, $Q = -1$ for Fr,
Table 4.1: Electronegativity (χ), interface coverage (C), interface Si charge state (Q), the calculated Schottky barrier height (S_{calc}), and the experimental Schottky barrier heights (S_{fit}, S_{width}, S_{expt}) for the metals used for Si termination (Ag, In, Au, and Pb) and for three other relevant hypothetical cases (Fr, Si, and F). The net experimental Schottky barrier height (S_{expt}) is the weighted average of the measurements derived from the quantum well energy fit (S_{fit}) and the peak width analysis (S_{width}) for each system.

<table>
<thead>
<tr>
<th>Element</th>
<th>χ</th>
<th>C</th>
<th>Q</th>
<th>S_{calc} (eV)</th>
<th>S_{fit} (eV)</th>
<th>S_{width} (eV)</th>
<th>S_{expt} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fr</td>
<td>0.68</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>0.54±0.07</td>
<td>0.59±0.08</td>
<td>0.55±0.05</td>
</tr>
<tr>
<td>Ag</td>
<td>1.47</td>
<td>1</td>
<td>-1</td>
<td>0.05</td>
<td>0.53±0.08</td>
<td>0.57±0.10</td>
<td>0.55±0.06</td>
</tr>
<tr>
<td>In</td>
<td>1.76</td>
<td>0.33</td>
<td>-0.05</td>
<td>0.55</td>
<td>0.50±0.04</td>
<td>0.54±0.03</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>1.87</td>
<td>0.42 (5×2)</td>
<td>-0.06</td>
<td>0.48</td>
<td>0.46±0.05</td>
<td>0.48±0.04</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>1.87</td>
<td>0.76 (√3-α)</td>
<td>-0.17</td>
<td>0.48</td>
<td>0.46±0.03</td>
<td>0.34±0.12</td>
<td>0.45±0.03</td>
</tr>
<tr>
<td>Au</td>
<td>1.87</td>
<td>0.96 (√3-β)</td>
<td>-0.24</td>
<td>0.44</td>
<td>0.48±0.05</td>
<td>0.48±0.07</td>
<td>0.48±0.04</td>
</tr>
<tr>
<td>Si</td>
<td>2.28</td>
<td>1</td>
<td>0</td>
<td>0.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>2.41</td>
<td>1</td>
<td>0.08</td>
<td>0.62</td>
<td>0.62±0.06</td>
<td>0.59±0.07</td>
<td>0.61±0.05</td>
</tr>
<tr>
<td>F</td>
<td>3.91</td>
<td>1</td>
<td>1</td>
<td>1.15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The most electropositive element. For Si termination, Q = 0 as expected, meaning that the charge state remains neutral. No Q value can be calculated for the Ag interfactant because the Ag-√3×√3 reconstruction sits on a half-bilayer of the Si(111) substrate and its concentration is not directly comparable to that of the other reconstructions, all of whose structures incorporate a full Si bilayer.

Also included in Table 4.1 are the calculated Schottky barrier heights based on a linear mapping from the Q scale:

\[ S_{calc} = \frac{Q + 1}{2} E_g, \]  

(4.4)

where 1.15 eV is the Si gap at 100 K. The mapping is linear because the charge state Q is proportional to the interface dipole, which contributes directly to the barrier height. The coefficients of the mapping are verified as follows. Considering F termination, the Si layer in direct contact is in the +1 charge state (but not the next layer). This means that the Fermi level at the interface must be pinned at the conduction band edge, resulting in an ionized interface Si layer. For the n-type substrates used in this experiment, \( S = E_g \), and this is exactly what Equation (4.4) yields. Likewise, for Fr termination, where the Si layer at the interface is in a -1 charge state, \( S = 0 \) based on similar physical arguments, and this is also what Equation (4.4) yields.

The calculated Schottky barriers from Equation (4.4) for the interfacant systems are included in Table 4.1 for comparison. The results are also shown in Figure 4.9 where the measured Schottky barrier heights (dots)
Figure 4.9: Experimental (circles) and predicted (line) Schottky barrier heights plotted against the interface Si charge parameter $Q$.

are compared with the calculated barrier heights (line) as a function of the interfacial Si charge state $Q$. The agreement is very good in that the calculation reproduces the overall trend and its correlation with $Q$. This level of quantitative agreement is remarkable considering the simplicity of the model which involves only the known chemical composition of the interface and the well established electronegativity table.

4.4.2 Interfactant Concentration Dependence

Further validation of the model can be observed by fixing the chemical species so that the only variable parameter is the interfactant concentration. This is achieved by focusing on the Pb films grown on the multiple Au/Si(111) surface reconstructions. Au adsorption onto the Si(111) surface yields different reconstructions depending on the amount deposited and the annealing conditions. This allows for a comparison across several well-characterized gold-terminated surfaces at different interfactant concentrations [24]. Multiple Au/Si(111) reconstructions can coexist, so the surface RHEED patterns were monitored during sample preparation to ensure single-phase coverage. As discussed in the previous section, the quantum well energy levels for films grown on the four Au-terminated surfaces studied are shown in Figures 4.2 and 4.6.

The $6\times6$ and $\text{Au-}\sqrt{3}\times\sqrt{3} - \beta$ reconstructions are formed at the same Au coverage but are reached through different annealing conditions following deposition, with the former resulting from a slow cool and the latter
forming from a rapid quench. These periodicities have different structural arrangements on the Si surface, but the same Au concentration, and so in the context of the interface dipole model should give rise to the same charge rearrangement, quantum well energies, and Schottky barrier height. Figure 4.10 directly compares the energy levels measured for Pb films on the Au-6×6 and Au-3√×3 – β terminated Si surfaces as a function of thickness. The quantum well energies of the two systems are very close, as predicted.

The experimentally determined Schottky barrier heights for the two systems also exhibit equality as seen in Figure 4.11, which compares the measured Schottky barrier heights (dots) with the calculated barrier heights (line) as a function of the interfacial Au concentration $C_{Au}$. The data point for Pb films grown on the Pb-3√×3 surface is included as a reference for $C_{Au} = 0$. Once again, the calculation reproduces both the overall trend and its correlation with $C_{Au}$.

4.5 Conclusions

To recap, the “surface sensitive” technique of valence band photoemission has been used in a novel manner to probe the Schottky barrier by exploiting the interface dependence of quantum wells. This study shows that metal termination of Si surfaces prior to film deposition can be an effective means for Schottky barrier engineering. The electronegativity of the metal, together
with the coverage, determines a net charge transfer. The resulting interface dipole layer gives rise to a potential difference directly contributing to the barrier. An important insight derived from the present study is that the charge state of the interfacial Si can be directly tied to the barrier height, without any assumptions about the thickness of the dipole layer and the effective dielectric constant at the interface as have been discussed extensively in the literature [40–42]. This insight and the predictive power of the model are of value to barrier engineering at the atomic level.

Figure 4.11: Experimental (circles) and predicted (line) Schottky barrier heights plotted against the interface Au concentration $C_{Au}$. 
5 Thermal Stability Control

5.1 Overview

Compared to the macroscopic systems that are commonly found in current solid-state electronic devices, nanoscale systems exhibit an increased sensitivity of properties to atomic-scale variations in size. A single monolayer fluctuation has a non-negligible effect on a film when the change is significant relative to the total film thickness. The resultant alteration in electronic structure will propagate through to other electronic and physical properties, such as stability temperature, that on larger length scales appear to be independent of thickness. If ultrathin films are to be of use in the miniaturized devices of the future, it is critical to identify means to control these thickness-sensitive properties at the quantum level.

The capacity to tune the electronic structure of metal films by using interfactants to modify the boundary condition at the interface suggests that interfacial engineering can also be used to influence the film thermal stability. Extending the examination of interfactant effects to explore this possibility, thermal stability temperatures are measured over a range of thicknesses for Pb films prepared on three different metal-terminated Si(111) surfaces, with In, Au, and Pb being the interfactants. The layer-by-layer changes in film electronic energy arising from the quantized Pb(111) electronic structure cause the thermal stability of the films to oscillate with an approximate bilayer period. While the bilayer oscillations, being related to the electronic structure of Pb, are not expected to change, the phase of the oscillations, being sensitive to the boundary conditions, should be amenable to modification by the use of interfactants. Indeed, a comparison of the three systems reveals that interfacial engineering can control the phase and amplitude of the stability oscillations. The phase of the oscillation is seen to differ markedly among the three cases by as much as \( \pi \), thus implying a phase reversal. Specifically, Pb films on In/Si(111) made of odd numbers of atomic layers \((N = 5, 7, \text{ and } 9 \text{ ML})\) are more stable than the even ones, while the other two systems exhibit greater stability for even thicknesses. Additionally, films grown on the Au-6×6 interfactant-terminated substrate exhibit
maximum stability temperatures in excess of room temperature. These results are interpreted in the context of the varying phase shifts experienced by the confined Pb electrons at the substrate interface. This work therefore demonstrates that quantum control of physical properties is feasible via interfacial engineering, and the results shed light on the relationship between the electronic structure and thermal stability [66].

5.2 Thickness-Dependent Oscillations in Pb

The confinement of an atomically thin film’s electrons by its boundaries gives rise to quantum well states. The total electronic energy of the system can change substantially and non-monotonically as a function of the film thickness.
thickness $N$ in terms of monolayers as a result of these discrete electronic states. For Pb films deposited on Si(111), the summation of occupied subbands causes the electronic energy to oscillate as a function of film thickness $N$ with an approximately bilayer period [38,67]. The situation is similar to the shell effect associated with elements in the periodic table - periodic filling of the atomic shells with increasing atomic number leads to periodic property variations. In thin films with increasing film thicknesses, the electrons fill one-dimensional "shells" that correspond to the quantum well states or subbands, and the properties oscillate for the same reason.

The thermal stability of the film is related to the total electronic energy or, more specifically, to the second derivative of the total energy as a function of the film thickness [38]. This derivative is related to the surface energy of the film and its oscillatory behavior is expected to be reflected in that of the stability temperature [25,67–69]. Figure 5.1 displays the calculated surface energy for a Pb(111) film based on a free-electron gas confined to an infinite quantum well [67]. The thickness-dependent oscillations have a period of $\Delta N = \lambda_F/(2t) = \pi/(k_F t)$, where $t$ is the interlayer spacing, $\lambda_F$ is the metal’s Fermi wavelength, and $k_F$ is the Fermi wave vector. For Pb(111), the oscillation period is 2.2 ML. The physical implications of this non-integer period are discussed further in Section 5.4. In addition to the thermal stability temperature, a host of other Pb film properties are also expected to oscillate under the influence of electron confinement: the work function, the charge density distribution, the interlayer lattice spacing, and the superconducting critical temperature [38,70–72]

### 5.3 Quantum Well Spectroscopy Redux

In our experiment, the In-, Au-, and Pb- terminated Si(111) surfaces were prepared as before by depositing appropriate amounts of the materials onto Si(111)-(7×7) followed by annealing to yield the $\sqrt{3} \times \sqrt{3}$-r, 6×6-, and $\sqrt{3} \times \sqrt{3}$-reconstructed surfaces with corresponding coverages of 0.33, 0.96, and 0.33 monolayers (ML), respectively [23–25,62]. Thin Pb films were then grown over the substrates at 60 K. The low substrate temperature during deposition was essential for forming smooth films. The resulting Pb films were oriented along the (111) direction with a film lattice constant that was bulk-Pb-like and incommensurate with the Si substrate lattice.

The measured quantum well state energies for Pb films grown on the In-, Au-, and Pb-terminated surfaces as a function of film thickness at normal emission from the previous chapter are re-presented in Figure 5.2. Boxes in
the figure enclose quantum well states at the same Pb film thickness and with the same quantum number \( n \) for the three different substrate terminations. Recall that the quantum well energy levels are determined by the Bohr-Sommerfeld quantization rule \([35-37]\)

\[
2k(E)Nt + \phi_n + \phi_i = 2n\pi, \tag{5.1}
\]

where the interface phase shift, which can depend on the interfactant, is given over a limited energy range near the valence band maximum of Si at \( E_0 \) by

\[
\phi_i(E) = A + B\sqrt{E - E_0} \Theta(E - E_0) \tag{5.2}
\]

where \( B \) is a constant related to the electronic structure of Si near the band edge [62]. Both the band edge \( E_0 \) and the constant \( A \) can depend on the interfactants used, but the differences in \( \phi_i \) among the three cases are mostly caused by variations in \( A \).

The simultaneous fit of observed quantum well energy levels performed in the Schottky barrier analysis using Equations (5.1) and (5.2) yields \( A = -1.70, 0.29, \) and 2.21 for the In, Au, and Pb interfactant systems, respectively. The difference between the In and Pb cases is close to \( \pi \), suggesting
that the two systems are nearly out of phase in regard to quantum well properties. Indeed, an inspection of Fig. 5.2 shows that the energy levels closest to the Fermi level for Pb/In/Si(111) at thicknesses \( N \) nearly interlace the corresponding levels for Pb/Pb/Si(111) at \( \Delta N = \pm 1 \). In other words, the observed differences are equivalent to a change in film thickness by one monolayer. Since the Fermi wave vector \( k_F \) of Pb is nearly halfway between the zone center and the zone boundary \([38]\), \( 2k \approx \pi \) in Eq. (5.1), and \( \Delta N = 1 \) is equivalent to a phase change of \( \pi \).

### 5.4 Thermal Stability Temperature

#### 5.4.1 Experimental Measurement

The thermal stability of the films is experimentally determined by the threshold temperature during annealing at which the film geometry begins to change and roughen. The photoemission peak intensity for the quantum well state associated with a specific film thickness is monitored as a function of increasing temperature. In the experiments conducted for this thesis, the sample was heated at the rate of \( \sim 1 \) K/min. A set of typical results is presented in Figure 5.3 for a Pb film with \( N = 8 \) grown on the In-\( \sqrt{3} \times \sqrt{3} \)/Si(111) surface. Figure 5.3(a) shows that at increasing temperatures the \( N = 8 \) photoemission peak intensity decreases and a new peak corresponding to \( N = 9 \) emerges. Figure 5.3(b) is a plot of the intensity of the \( N = 8 \) peak. It displays a sudden drop, corresponding to the point at which the film irreversibly changes into one with multiple thicknesses including \( N = 9 \). The roughening transformation or stability temperature is found by the intersection of linear fits to the data as indicated in Figure 5.3(b).

The measurement process is time-intensive because the roughening transformation is irreversible, requiring a new film sample to be prepared \textit{in situ} from a fresh Si(111) surface for each interfacant and for each film thickness.

#### 5.4.2 Stability Analysis

The measured stability temperatures at various thicknesses for each interfacant are displayed in Figure 5.4. All three systems exhibit the bilayer thickness-dependent oscillations characteristic of many Pb film physical properties \([25,38,67,71,72]\). These oscillations arise from the periodic crossing of the Fermi level by the quantum well states (or subbands) with increasing thickness. At each crossing, a new subband moves below the Fermi level and begins to be filled by the increasing number of electrons.
Figure 5.3: (a) Photoemission spectra for a Pb film of coverage \( N = 8 \) ML grown on In-terminated Si(111) at various annealing temperatures as indicated. At higher temperatures, the film breaks up to form multiple thicknesses including \( N = 9 \). (b) Peak intensity as a function of annealing temperature for the \( N = 8 \) peak. The straight line segments are linear regressions to the data and their intersection point indicates the temperature at which the film breaks up.
This produces a change in the overall electronic structure, and the physical properties should change correspondingly. As seen in Figure 5.2, the \( n = 2, 3, \) and 4 states move below the Fermi level at approximately 2 ML period. More precisely, the crossing points are evenly spaced at 2.2 ML, one-half the Fermi wavelength. This gives the appearance over short thickness ranges of an oscillation with a 2 ML period. Over wider ranges this non-integer period produces a beating effect in which there is a relative phase reversal every 9 ML. Such a reversal can be seen in the Pb/Pb/Si(111) case at \( N \approx 4, \) which corresponds to a nodal point in the beating envelope function where the bilayer oscillation amplitude is suppressed.

While the stability curves in Figure 5.4 show bilayer oscillations in all three cases, the amplitude and phase of the oscillations are significantly different. Specifically, Pb films made of odd numbers of atomic layers (5, 7, and 9) on In/Si(111) are more stable than the even ones. This trend is reversed for the other two cases. Also, the apparent amplitude of bilayer oscillations is much larger for Pb/Au/Si(111) than the other two cases. These results are related to the different electronic structures discussed above, and will be analyzed below.

Since Pb has a free-electron-like electronic structure, we expect the thickness-dependent oscillations in stability temperature to follow a simple Friedel-like functional form [38, 67, 71]:

\[
T(N) = C \frac{\sin(2k_F tN + \Phi)}{N^\alpha} + D + F, \tag{5.3}
\]

where \( \Phi \) is a phase shift that depends on the boundary conditions or interfactants used. Equation (5.3) is used to fit the stability data for all three systems. The exponent \( \alpha \) should be independent of the boundary conditions. The fit is actually insensitive to the choice of \( \alpha \) over a wide range, and thus we have used a fixed value of \( \alpha = 1.77 \) deduced from a free-electron model [67]. The constants \( C \) and \( D \) should be the same for all three systems, while \( F \), which is related to the absolute interface energies, can depend on the interfactants used.

The fits are presented in Figure 5.4, where the dashed curves are the envelope functions derived from Equation (5.3) for the 9-ML beating pattern [67]. The effect of \( F \) is an overall shift of the stability temperature curve. Thus, \( \Phi \) is the only interfactant-dependent parameter that controls the differences in the amplitude and phase of the oscillations among the three cases. The good fits achieved are a confirmation of the free-electron-like behavior of the Pb quantum wells. As noted above, the bilayer oscillation amplitude
Figure 5.4: Annealing temperature as a function of thickness at which Pb films grown on In-, Au-, and Pb-terminated Si(111) become unstable. Also shown are fits to the results. The dashed curves indicate the envelope functions of the fits.
for Pb/Au/Si(111) appears to be much larger than the other two cases, even though the parameters $C$ and $D$ are the same for the three systems. This difference can be understood in terms of $\Phi$. For Pb/Au/Si(111), the system’s phase shift causes the integer thickness sampling of the Friedel-like function to occur near the extremes, producing a large amplitude of oscillations. For the other two systems, the Friedel-like function is sampled away from the extremes, and thus the amplitude of oscillations is suppressed.

### 5.5 Phase Comparison

Comparing the phase factor of the sinusoidal function in Equation (5.3) with the left-hand side of Equation (5.1) reveals that $\Phi$ is directly related to $\phi_s + \phi_i$ at the Fermi level. This is simply a restatement that physical properties are expected to vary each time a new quantum well state or subband crosses the Fermi level. As discussed above, the Pb/In/Si(111) case has an electronic structure resembling that of Pb/Pb/Si(111) at thicknesses differing by $\Delta N = 1$. Thus, films of odd $N$ for Pb/In/Si(111) should behave similarly to films of even $N$ for Pb/Pb/Si(111). This is the underlying reason for the stability phase reversal. This behavior can also be explained in terms of the phase shift. A change in film thickness by $\Delta N = 1$ is equivalent to a phase change in $\phi_s + \phi_i$ by $\pi$, which, in turn, is equivalent to a phase change in $\Phi$ by $\pi$. The latter, through Equation (5.3), corresponds to a phase reversal of the stability oscillations.

Table 5.1 and Figure 5.5 directly compare $\Phi$ to $\phi_s(E) + \phi_i(E)$ at the Fermi level for all three systems. It can be seen that if the two phases are linearly related then $\Phi$ will lag $\phi_s(0) + \phi_i(0)$ by $\sim \pi/2$ or roughly a quarter of a cycle. This relationship implies that the phase shift $\Phi$ governing the film thermal stability behavior can be determined by a simple examination of the quantum well states within the film.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Phi$</th>
<th>$\phi_s(0) + \phi_i(0)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>-1.354</td>
<td>-3.435</td>
</tr>
<tr>
<td>Au</td>
<td>0.942</td>
<td>-1.373</td>
</tr>
<tr>
<td>Pb</td>
<td>1.529</td>
<td>0.337</td>
</tr>
</tbody>
</table>

Table 5.1: Thermal stability oscillation phase factor $\Phi$ and quantum well electronic phase shift $\phi_s + \phi_i$ evaluated at the Fermi level for Pb(111) films grown on In-$\sqrt{3} \times \sqrt{3}$, Au-6×6, and Pb-$\sqrt{3} \times \sqrt{3}$ terminated Si(111).
5.6 Conclusions

In recapitulation, thermal stability of thin films can be controlled through the use of interfactants. Our results demonstrate that unstable film thicknesses can be turned into stable ones. This capability is important for developing strategies for device applications. The underlying physics of stability control can be traced to the sensitivity of quantum well electronic structure to the boundary conditions. For Pb films grown on In-, Au-, and Pb-terminated Si(111), the quantum well energy levels differ by as much as \( \sim 1 \) eV. The resulting electronic energy differences affect the thermal stability. Specifically, Pb films of odd \( N \) (5, 7, and 9) on In/Si(111) are more stable than the even ones. This trend is reversed for the other two cases. Also, the Pb/Au/Si(111) systems shows a much larger bilayer oscillation amplitude than the other two cases. These results illustrate, at the quantum mechanical level, the relationship between physical properties and electronic structure of thin films.
Recapitulation and Future Developments

This dissertation has presented research about the effect of interfactants on the properties of thin Pb films deposited on metal-terminated Si(111). These properties were probed experimentally with photoemission spectroscopy and the data were analyzed and interpreted in the context of theoretical models based on quantum mechanical and chemical considerations. The standard quantum well picture of electron confinement within a film predicts the existence of discrete electronic states whose energy levels depend on the film thickness and boundary conditions. Changes made to the film-substrate interface alter the characteristic film electronic structure and subsequently propagate through to other film properties. By isolating the interface effect on the properties, the experimental results confirm these predictions. In a study of layer-resolved films grown on a variety of interfactant-terminated Si(111) surfaces, the quantum well energy levels were measured over a wide range of film thicknesses and the Schottky barrier heights were extracted for each system. A comparison of the measured barrier heights to values calculated from an interface dipole model reveals that the Schottky barrier can be tuned to a desired height by selecting an interfactant with the appropriate electronegativity and concentration. In another experiment, the interfactant influence on the film energetics was studied by annealing Pb films and measuring the thermal stability temperatures. The stability temperatures exhibited a thickness-dependent oscillation with a quasibilayer period whose phase and amplitude varied with the interfactant. The phase differences in the thermal stabilities among the different interfactant systems were observed to directly correlate to the phase differences in the quantum well energy levels. Taken as a whole, these results demonstrate that the electronic and physical properties of thin films can be controlled at a quantum level through interfacial engineering.

Thin films are both model systems for the study of quantum effects as well as the building blocks of solid-state electronics and, as such, this body of research can serve as the foundation for future investigations in both the purely scientific and the technologically applied spheres. One course of study that would benefit both fields would be a continued effort to identify addi-
tional components of the film-substrate phase shift with physical parameters. The energy confinement range, via the Schottky barrier height, is directly determined by the concentration and electronegativity of the interfactant; if the interface phase constant term were defined in terms of a similar set of adjustable quantities, the total interface phase shift could be controlled in the laboratory. A possibility is that the origin of the phase constant lies within structural considerations such as lattice mismatch and strain at the interface, thus making it a candidate to be probed with x-ray diffraction. The capacity to manipulate the total phase would allow researchers and engineers to tailor a film’s properties with wide latitude. Another research direction would be to explore the effect of boundary modification as it pertains to the film-vacuum interface. Surfactants are commonly used during film deposition as a means to control growth morphology by minimizing surface energy. An investigation of surfactant effects on film energetics and physical properties would provide further validation of the quantum well model of electron confinement and would likely yield additional methods to alter film behavior. A third path is to identify additional film properties that can be controlled through interface modification. For example, recent work has shown that the superconducting critical temperature of thin Pb films oscillates as a function of film thickness, suggesting a dependence on the quantum electronic structure. The potential therefore exists to manipulate the critical temperature and obtain specific superconducting behaviors using interfactants.

To conclude, the quantum electronic structures and related properties of nanoscale films can directly be controlled through interfacial engineering. This ability will facilitate future technological advances, bringing us one step closer to harnessing the potential of the quantum world for practical purposes.
References


[28] Photograph provided by Yang Liu.


Author’s Biography

Dominic Anthony Ricci was born on December 20, 1977, and after residing in Yonkers, New York until the age of three, moved to New Fairfield, Connecticut, where he spent his formative years. He graduated with a bachelor of science in physics from the Massachusetts Institute of Technology in 1999. He received a M.S. in physics from the University of Illinois at Urbana-Champaign in 2002 and his Ph.D. in 2006.

Publications


