As electronic device miniaturization descends further toward the atomic realm it becomes increasingly imperative to comprehend the quantum physics that dominates the regime. Thin films are the basic building blocks for solid-state devices, and their simple geometry makes them ideal models for fundamental scientific studies. When the thickness of a film decreases to the atomic scale, the confinement of the film’s electrons by its boundaries gives rise to discrete electronic states. These quantum well states cause the electronic and physical film properties to deviate sharply from those of bulk systems. Controlling these characteristics at a quantum level is critical for thin film applications. Interfactants can modify 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 Pb films grown on several metal-terminated Si(111) surfaces [1]. By maintaining the same film and substrate while varying the interfactant, we have isolated the interface effect upon the Schottky barrier, 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 metals used for termination include Ag, In, Au, and Pb, and the resulting barrier heights are significantly different among the four systems. Total confinement occurs for electrons with energies within the confinement range $E_0$ between the metal Fermi level and the Si valence band maximum. For $n$-type substrates, the Schottky barrier height is the difference between the semiconductor energy gap and the confinement energy, so a measurement of $E_0$ is a measurement of the barrier.

Quantum well states are characterized by discrete energies that are highly sensitive both to film thickness and interface conditions [2]. 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 appear as sharp, intense peaks in photoemission spectra, as exhibited by the data in Fig. 1 from Pb films grown at 100 K on the Au-6×6 reconstructed Si(111) surface. These peaks are fully developed at integer monolayer thicknesses and the atomic layer resolution permits a determination of the absolute film thickness by atomic layer counting. Similar spectra were taken for films grown on Ag-$\sqrt{3} \times \sqrt{3}$, In-$\sqrt{3} \times \sqrt{3}$, and Pb-$\sqrt{3} \times \sqrt{3}$ terminated Si(111) substrates. The energies of quantum well states are governed by the Bohr-Sommerfeld quantization rule such that the sum of the phase accumulated by an electron traversing the film and the phase shifts it experiences at the film-substrate and film-vacuum interfaces must be an integer multiple of $2\pi$ [2]. The phase accumulated in the film is dependent upon the Pb
band structure and is known from first-principles calculations, as is the phase shift at the vacuum [3]. The substrate phase shift is modeled with the sum of a constant term and a singularity at the valence band maximum [4]. We fit the observed quantum well energy levels for all four systems simultaneously and thus obtain both $E_0$ and the Schottky barrier height for each set of films. The quantum well state energies generated from this fit for the Pb/Au-6×6/Si(111) system are displayed in Fig. 1 as superimposed circles.

![Figure 1](image)

**Figure 1.** Photoemission intensity as a function of energy and film thickness for Pb films deposited on the Au-6×6 terminated Si(111) surface. The normal emission spectra were taken with photon energy = 22 eV. The intensity maxima (brighter regions) correspond to quantum well states. The solid curves indicate the evolution of the quantum well energies based on a simultaneous fit to the data for all four systems. The quantum number $n$ for each branch is noted.

These results are complemented and confirmed by a measurement of the quantum well peak widths, which provides an independent determination of the Schottky barrier heights. States in the quantum well that are 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. In each case, the measured width exhibits a threshold in energy below which it increases rapidly.

An analysis of the results establishes that a simple chemical model can describe the interface component of the Schottky barrier height. The electronegativity and concentration of the metal used for Si termination determines the degree of charge transfer around the interfacial metal-semiconductor bonds. This rearrangement in turn gives rise to an interface dipole layer that determines the barrier height. We define a parameter $Q$ as the average charge state of the Si in direct contact with the interfacial metal layer. This parameter, which is proportional to the interface dipole, is the ratio of the difference between the coverage-weighted electronegativity for the interfacial metal layer and the electronegativity of Si to the difference between the extremes of the electronegativity scale. The Schottky barrier height is calculated with the parameter determining the deviation from the midpoint of the energy gap. The comparison of the measured and calculated values for the Schottky barrier height as a function of $Q$ demonstrates excellent agreement 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 that involves only the known chemical composition of the interface and the well-established electronegativity table. An important insight derived from this 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 [5]. The implication of these results is that it is possible to tune the Schottky barrier to a desired height through the judicious selection of a metal interfacant. For a given metal-semiconductor junction, this deterministic procedure depends only on the electronegativity and concentration of the interfacial chemical species.

![Figure 2](image)

**Figure 2.** Annealing temperature as a function of thickness at which Pb films grown on Pb-, In-, and Au-terminated Si(111) become unstable. Also shown are fits to the results (crosses).

We have extended our technique of quantum well spectroscopy to examine the interfacant effect on film thermal stability [6]. The thermal stability temperature is the threshold annealing temperature at which the film structure begins to roughen. This physical parameter is relevant to the film’s robustness under technological application operating conditions. When a smooth layer-resolved film breaks down due to increasing temperature, the quantum well peak intensity displays a sudden drop from which the thermal stability temperature is extracted.

Thermal stability temperatures were measured over a range of thicknesses for Pb films grown on the In, Au, and Pb terminated Si(111) surfaces. As seen in Fig. 2, all three systems exhibit the approximate bilayer thickness-dependent oscillations characteristic of
many Pb film physical properties. These oscillations arise from the periodic crossing of
the Fermi level by the quantum well states with increasing thickness. The relative
amplitudes and phases differ significantly among the systems. While Pb films made of
odd numbers of atomic layers on In/Si(111) are more stable than the even ones, this trend
is reversed for the other two cases. The amplitude of the bilayer oscillations is also much
larger for Pb/Au/Si(111) than the other two cases. These stability behaviors reflect the
differing electronic structures among the systems produced by the interfactants.

The Pb/In/Si(111) system has an electronic structure resembling that of
Pb/Pb/Si(111) at thicknesses offset by one atomic layer. Each interfactant creates a
unique electronic phase shift at the substrate boundary. The phase shift parameters
derived from a fit of the thermal stability curves with a simple Friedel-like functional
form compare well to the phase shift constants calculated in the Schottky barrier quantum
well energy analysis. The phase shift difference between the Pb/In/Si(111) and
Pb/Pb/Si(111) systems is found to be roughly $\pi$ through both methods, which corresponds
to the phase reversal of the stability oscillations. These results demonstrate that the
thermal stability of thin films can be controlled by means of interfactants.

Our experiments elucidate the sensitivity of the quantum well electronic structure
to the boundary conditions. These findings offer important insight into and predictive
power about the basic atomic-level physics of thin film electronic and physical properties
that are important to the future of device applications.

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