

Controlling the Thermal Stability of Thin Films by Interfacial Engineering

D. A. Ricci, T. Miller, and T.-C. Chiang

Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080, USA
Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, 104 South Goodwin Avenue, Urbana, Illinois 61801-2902, USA

(Received 23 September 2005; published 19 December 2005)

The quantized electronic structure in Pb films on Si(111) varies substantially as the film thickness increases. The changes in electronic energy cause the thermal stability of the films to oscillate with an approximate bilayer period. The phase of the oscillations can be controlled by interfacial engineering. Comparison of Pb films prepared on Si(111) terminated by In, Au, and Pb as interfactants reveals a phase reversal. For Pb/In/Si(111), films made of odd numbers of atomic layers (5, 7, and 9) are more stable than the even ones. This trend is reversed for the other two cases.

DOI: [10.1103/PhysRevLett.95.266101](https://doi.org/10.1103/PhysRevLett.95.266101)

PACS numbers: 68.60.Dv, 73.21.Fg, 73.30.+y, 79.60.Dp

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 of special interest in this regard as they are the basic building blocks for devices, and their simple geometry makes them ideal models for fundamental scientific studies. As 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, known as quantum well states [1–3]. As a result, the total electronic energy of the system can change substantially and non-monotonically as a function of the film thickness N in terms of monolayers. For Pb films deposited on Si(111), the system investigated in this work, the electronic energy is expected to oscillate as a function of film thickness N with an approximately bilayer period. The thermal stability of the film, which is related to the total energy (or the second derivative of the total energy as a function of film thickness), is expected to oscillate correspondingly [4–7]. In fact, a host of other physical properties are also expected to oscillate [8,9]. 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.

A critical issue for thin film applications is property control at the quantum level. This Letter explores the use of interfactants to modify the boundary condition at the interface and thereby to modify the electronic structure and thermal stability. Specifically, we compare Pb films, with the same thickness, prepared on three interfactant-terminated Si(111) surfaces, with In, Au, and Pb being the interfactants. 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 modifica-

tion by the use of interfactants. Indeed, the phase of the bilayer stability oscillation is seen to differ markedly among the three cases by as much as π , thus implying a phase reversal. Specifically, Pb films on In/Si(111) made of odd numbers of atomic layers ($N = 5, 7, \text{ and } 9$) are more stable than the even ones. This trend is reversed for the other two cases. 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.

In our experiment, the In-, Au-, and Pb-terminated Si(111) surfaces were prepared by depositing appropriate amounts of the materials onto Si(111)-(7 × 7) followed by annealing to yield the $\sqrt{3} \times \sqrt{3}$ -, 6×6 -, and $\sqrt{3} \times \sqrt{3}$ -reconstructed surfaces with corresponding coverages of 0.33, 0.96, and 0.33 monolayers (ML), respectively [4,10–12]. 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. The film lattice constant was bulk-Pb-like and incommensurate with the Si substrate lattice. The photoemission measurements were performed on undulator beam lines at the Synchrotron Radiation Center, University of Wisconsin, using 22 eV photons, in the same chamber wherein the films were prepared. Photoemission data were acquired with a Scienta SES100 hemispherical analyzer. The sample area probed by the synchrotron beam was $\sim 1 \text{ mm}^2$.

In photoemission spectra quantum well states appear as sharp peaks that reach maximum intensity at integer monolayer film thicknesses. This atomic-layer resolution allows a determination of the absolute film thickness by atomic-layer counting [4,13,14]. 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 are shown in Fig. 1. Boxes in the figure enclose quantum well states at the same Pb film thickness

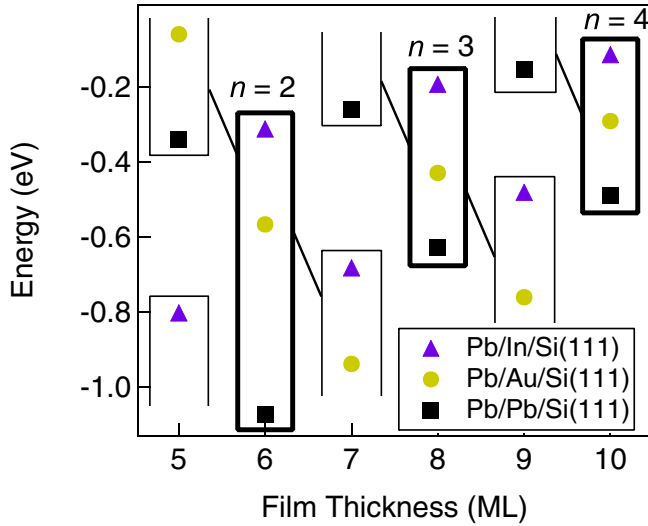


FIG. 1 (color online). Measured quantum well state energy levels for Pb films grown on the In-, Au-, and Pb-terminated Si(111) surfaces as a function of film thickness N . States are grouped by quantum number n using boxes for each thickness.

and with the same quantum number n for the three different substrate terminations. It is evident that the quantum well energy levels can vary by up to ~ 1 eV among the systems. These large energy differences imply a strong effect of the interfacants on the electronic structure of the system.

The quantum well energy levels are determined by the Bohr-Sommerfeld quantization rule [1–3]:

$$2k(E)Nt + \phi_s + \phi_i = 2n\pi, \quad (1)$$

where k is the electron momentum, E is the energy of the state, t is the monolayer thickness, and ϕ_s and ϕ_i are the energy-dependent phase shifts at the surface and interface, respectively. The bulk band dispersion $k(E)$ and the surface phase shift ϕ_s are known from a first-principles calculation [15]. The interface phase shift can depend on the interfacants. Over a limited energy range near the valence band maximum of Si at E_0 , it is given by

$$\phi_i(E) = A + B\sqrt{E - E_0}\Theta(E - E_0), \quad (2)$$

where B is a constant related to the electronic structure of Si near the band edge [10]. Both the band edge E_0 and the constant A can depend on the interfacants used, but the differences in ϕ_i among the three cases are mostly caused by variations in A .

A simultaneous fit of observed quantum well energy levels for all three systems using Eqs. (1) and (2) yields $A = -1.70, 0.29,$ and 2.21 for the In, Au, and Pb interfaciant systems, respectively. The difference between the In and Pb cases is close to π , suggesting that the two systems are nearly out of phase in regard to quantum well properties. Indeed, an inspection of Fig. 1 shows that the energy levels closest to the Fermi level for Pb/In/Si(111) at thicknesses N nearly interlace the corre-

sponding 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 1 ML. Since the Fermi wave vector k_F of Pb is nearly halfway between the zone center and the zone boundary [15], $2kt \approx \pi$ in Eq. (1), and $\Delta N = 1$ is equivalent to a phase change of π .

The thermal stability of the films is experimentally determined by the threshold temperature during annealing at which the film structure begins to change and roughen. In the experiment, the sample was heated at the rate of

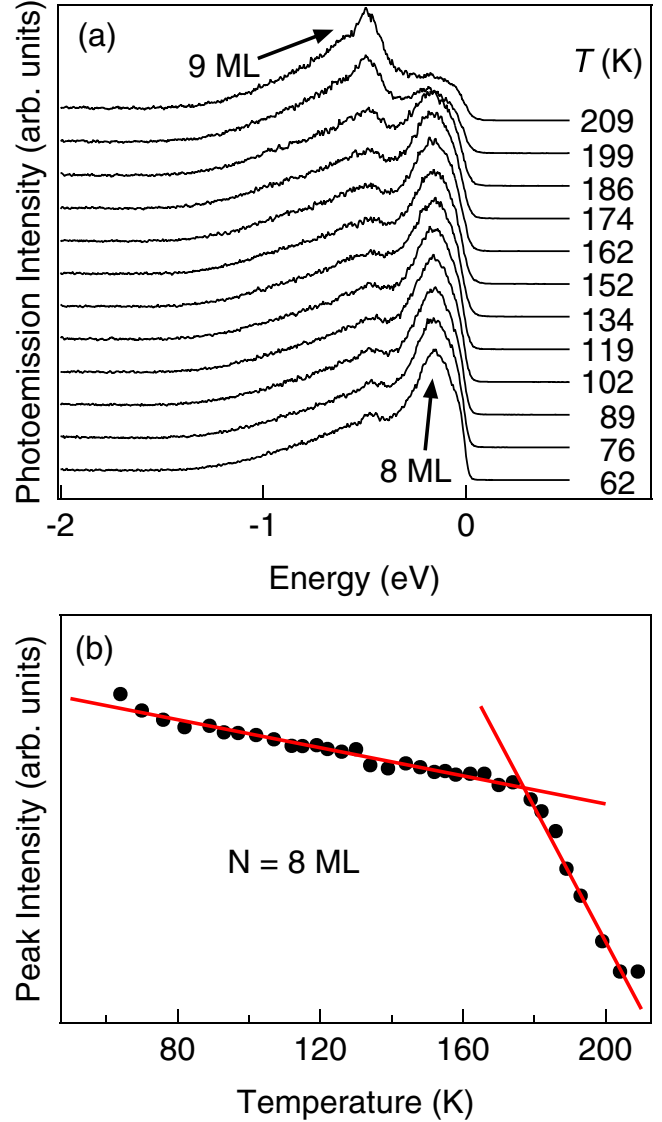


FIG. 2 (color online). (a) Photoemission spectra for a Pb film of coverage $N = 8$ ML grown on In-terminated Si(111) at various annealing temperatures as indicated. At higher temperatures, the film breaks up to form multiple thicknesses including $N = 9$. (b) Peak intensity as a function of annealing temperature for the $N = 8$ ML peak. The straight line segments are linear regressions to the data and their intersection point indicates the temperature at which the film breaks up.

~ 1 K/min. A set of typical results is presented in Fig. 2 for $N = 8$ on In-terminated Si(111). Figure 2(a) shows that at increasing temperatures the $N = 8$ photoemission peak intensity decreases and a new peak corresponding to $N = 9$ emerges. Figure 2(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 Fig. 2(b). The measurement process is time intensive because the roughening transformation is irreversible, requiring a new film sample to be prepared *in situ* from a fresh Si(111) surface for each interfactant and for each Pb film thickness.

The measured stability temperatures at various thicknesses for each interfactant are displayed in Fig. 3. All three systems exhibit the bilayer thickness-dependent oscillations characteristic of many Pb film physical properties [4,5,8,9,15]. 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. This produces a change in the overall electronic structure, and the physical properties should change correspondingly. As seen in Fig. 1, the $n = 2, 3,$ and 4 states move below the Fermi level at approximately 2 ML intervals. More precisely, the crossing points are evenly spaced at 2.2 ML, one-half the Fermi wave length. This gives the appearance over short thickness ranges of an oscillation with a 2 ML period. Over wider ranges this noninteger 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 Fig. 3 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 [5,8,15]:

$$T(N) = C \frac{\sin(2k_F t N + \Phi) + D}{N^\alpha} + F, \quad (3)$$

where Φ is a phase shift that depends on the boundary conditions or interfactants used. Equation (3) is used to fit the stability data for all three systems. The exponent α should be independent of the boundary conditions. The fit is actually insensitive to the choice of α over a wide range, and thus we have used a fixed value of $\alpha = 1.77$ deduced from a free-electron model [5]. 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 Fig. 3, where the dashed curves are the envelope functions derived from Eq. (3) for the 9 ML beating pattern [5]. The effect of F is an overall shift of the stability temperature curve. Thus, Φ 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 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 under-

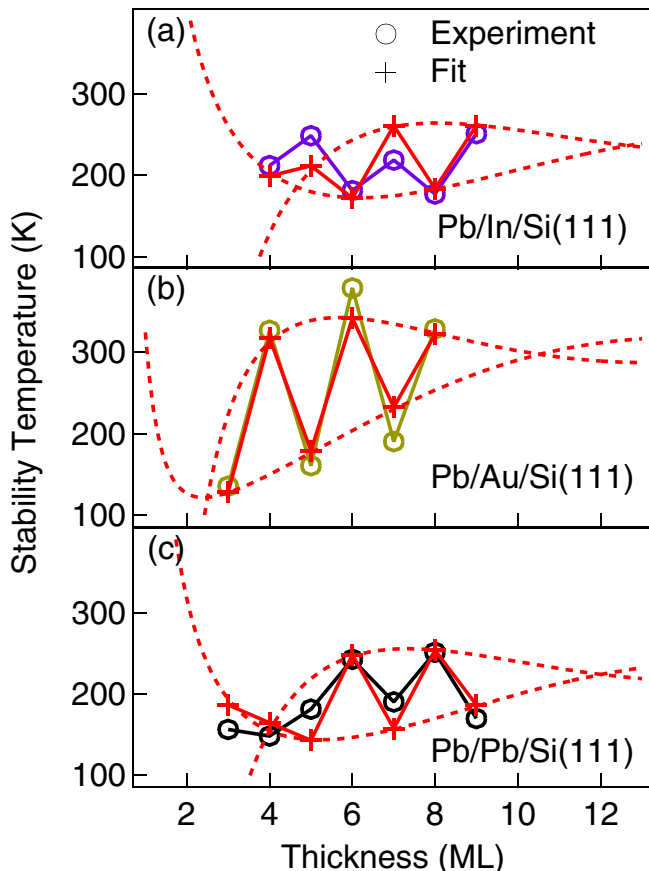


FIG. 3 (color online). Annealing temperature as a function of thickness at which Pb films grown on In-, Au-, and Pb-terminated Si(111) become unstable. Also shown are fits to the results. The dashed curves indicate the envelope functions of the fits.

stood in terms of Φ . 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.

Comparing the phase factor of the sinusoidal function in Eq. (3) with the left-hand side of Eq. (1) reveals that Φ 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 π , which, in turn, is equivalent to a phase change in Φ by π . The latter, through Eq. (3), corresponds to a phase reversal of the stability oscillations.

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 ~ 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 show 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.

This work is supported by the U.S. Department of Energy (Grant No. DEFG02-91ER45439). We acknowledge the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. National Science Foundation (Grant No. DMR-02-03003) for partial support of the synchrotron beam line operation. The Synchrotron Radiation Center of the University of Wisconsin-Madison is supported by the U.S. National Science Foundation (Grant No. DMR-00-84402).

-
- [1] T.-C. Chiang, Surf. Sci. Rep. **39**, 181 (2000).
 - [2] S.-A. Lindgren and L. Wallden, *Handbook of Surface Science, Vol. 2, Electronic Structure* (Elsevier, New York, 2000).
 - [3] M. Milun, P. Pervan, and D. P. Woodruff, Rep. Prog. Phys. **65**, 99 (2002).
 - [4] M. H. Upton, C. M. Wei, M. Y. Chou, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **93**, 026802 (2004).
 - [5] P. Czochke, H. Hong, L. Basile, and T.-C. Chiang, Phys. Rev. B **72**, 075402 (2005).
 - [6] M. C. Tringides and M. Hupalo, Phys. Rev. Lett. **94**, 079701 (2005).
 - [7] M. H. Upton, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **94**, 079702 (2005).
 - [8] T.-C. Chiang, Science **306**, 1900 (2004).
 - [9] Y.-F. Zhang, J.-F. Jia, T.-Z. Han, Z. Tang, Q.-T. Shen, Y. Guo, Z. Q. Qiu, and Q.-K. Xue, Phys. Rev. Lett. **95**, 096802 (2005).
 - [10] D. A. Ricci, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **93**, 136801 (2004).
 - [11] S. Mizuno, Y. O. Mizuno, and H. Tochiyama, Phys. Rev. B **67**, 195410 (2003).
 - [12] T. Nagao, S. Hasegawa, K. Tsuchie, S. Ino, C. Voges, G. Klos, H. Pfnur, and M. Henzler, Phys. Rev. B **57**, 10 100 (1998).
 - [13] J. J. Paggel, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **81**, 5632 (1998).
 - [14] M. H. Upton, T. Miller, and T.-C. Chiang, Appl. Phys. Lett. **85**, 1235 (2004).
 - [15] C. M. Wei and M. Y. Chou, Phys. Rev. B **66**, 233408 (2002).