

Thermal Stability and Electronic Structure of Atomically Uniform Pb Films on Si(111)

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Atomically uniform Pb films are successfully prepared on Si(111), despite a large lattice mismatch. Angle-resolved photoemission measurements of the electronic structure show layer-resolved quantum well states which can be correlated with dramatic variations in thermal stability. The odd film thicknesses $N = 5, 7,$ and 9 monolayers show sharp quantum well states. The even film thicknesses $N = 6$ and 8 do not, but are much more stable than the odd film thicknesses. This correlation is discussed in terms of a total energy calculation and Friedel-like oscillations in properties.

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Miniaturization of materials architecture has led to feature length scales approaching the nanoscale. Two important issues arise in this regime: one is the emergence of quantum mechanical effects associated with confinement and interference; the other is an increased sensitivity of properties to atomic-scale variations in size. Thin films are widely employed in device designs. A change in film thickness by just one atomic layer can result in property variations on the order of $1/N$, where N is the thickness of the film in terms of monolayers (ML). This can lead to interesting and important properties, and the present work is a demonstration of this effect in a simple model system, Pb films on Si(111).

We report on the thermal stability and the electronic structure as well as their relationship. Angle-resolved photoemission measurements show sharp and intense quantum well states [1–3] derived from Pb valence electrons confined in the film for odd film thicknesses $N = 5, 7,$ and 9 ML, but not for the intervening even film thicknesses $N = 6$ and 8 . The measured thermal stability is well correlated with these even-odd variations, with the $N = 6$ and 8 films being much more stable than the others. These observations, augmented by theoretical results, shed light on Friedel-like quantum oscillations in properties which are expected to be prevalent at the nanoscale.

The success of this experiment relies on the preparation of atomically uniform films. Despite the large lattice mismatch between Pb and Si, smooth growth is achieved by a special growth process. While previous studies of Pb on Si showed preferred island heights [4], thus hinting at stability variations, the present work goes further by providing quantitative stability data as a function of both thickness and temperature.

The experiment was performed at the Synchrotron Radiation Center, University of Wisconsin–Madison. Angle-resolved photoemission data were taken with a

Scienta analyzer equipped with a two-dimensional detector. The Si(111) substrates were prepared from n -type wafers with a resistivity of $1\text{--}60\ \Omega\ \text{cm}$. As shown by previous studies and by our own experimentation [4–9], direct deposition of Pb on the (7×7) reconstructed Si(111) at various temperatures always resulted in rough films. To prepare atomically uniform films, we first deposited approximately 2 ML of Pb on Si(111)- (7×7) . The sample was then annealed at above $400\ ^\circ\text{C}$ to desorb the Pb. The desorption curve, as measured by photoemission intensities of the Pb $5d$ and Si $2p$ core levels, exhibited breaks corresponding to the formation of distinct phases [9–11]. From previous studies, it is known that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ α phase forms at a residual Pb coverage of 1.1 ML (equivalent to $4/3$ ML of Si coverage). The $(\sqrt{3} \times \sqrt{3})R30^\circ$ β phase forms at a residual Pb coverage of 0.28 ML (equivalent to $1/3$ ML of Si coverage). Our experiment showed that atomically uniform films of Pb were obtained by depositing Pb on the α phase, the β phase, or any intermediate phases at 100 K. The final results were the same for the same total amounts of Pb deposition including the initial Pb coverages. The photoemission spectra shown below were obtained with the sample at 100 K, and the film thicknesses indicated are the total number of Pb monolayers in the film, excluding the initial β phase Pb coverages.

The three-dimensional plot in Fig. 1(a) shows the normal-emission intensity as a function of binding energy and film thickness. Three major peaks, at binding energies of 0.4, 0.26, and 0.15 eV below the Fermi level, attain their maximum intensities at film thicknesses $N = 5, 7,$ and 9 , respectively, while no such peaks are observed at the layer thicknesses $N = 6$ and 8 . These peaks are quantum well states formed by confinement of the Pb p -band electrons by the Si band gap [12,13]. No such quantum well states exist for $N = 6$ and 8 .

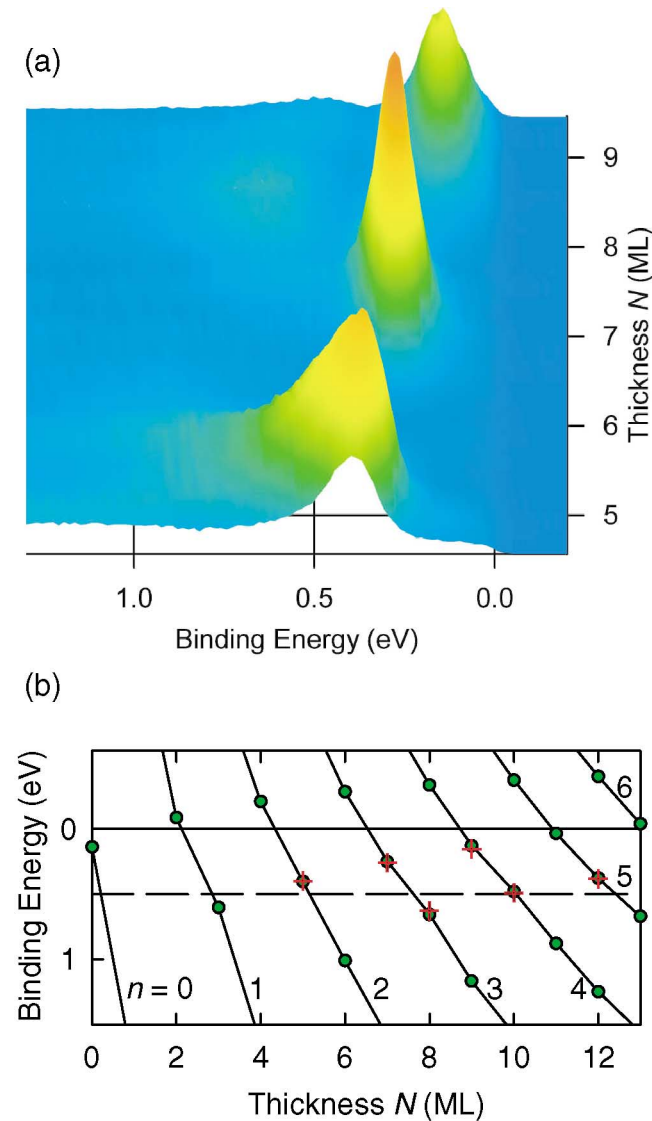


FIG. 1 (color). (a) Photoemission intensity as a function of Pb film thickness and binding energy. Three major quantum well peaks are seen at $N = 5, 7$, and 9 . A weak resonance peak at higher binding energy is seen at $N = 8$. (b) Binding energies of quantum well peaks (circles connected by lines) deduced from a fit to the experimental results (crosses). The quantum number n for each branch is indicated.

The appearance of intense peaks for odd N comes from the specific band structure of Pb and the Si band gap. From data taken over a wide thickness range, it is concluded that the Fermi level of the Pb is at 0.5 eV above the Si valence band edge. Electrons in the Pb film with binding energies within 0.5 eV of the Fermi level are confined by the Si band gap, giving rise to sharp and intense quantum well peaks. Electrons at higher binding energies are not confined. Nevertheless, partial reflection at the Pb-Si boundary can give rise to resonances which appear in photoemission as weak and broad peaks [2]. One such weak resonance peak at a binding energy of 0.63 eV can be seen in Fig. 1(a) at $N = 8$. From the confinement range of

0.5 eV and the known Si band gap of 1.2 eV, a Schottky barrier height of 0.7 eV is deduced for our n -type Si substrate. This is consistent with a recent reported value of 0.72 ± 0.02 eV based on electrical measurements [14].

The binding energies of quantum well states are determined by the Bohr-Sommerfeld quantization rule [1–3,12]:

$$2kNt + \phi_s + \phi_i = 2n\pi, \quad (1)$$

where k is the wave vector, t is the monolayer thickness, ϕ_s is the phase shift at the surface, ϕ_i is the phase shift at the interface, and n is a quantum number. This equation determines the allowed k values, which in turn determine the binding energies of the quantum well states through the band dispersion relation $E(k)$. The surface phase shift ϕ_s , as a function of energy, has been computed by a first-principles method [12], and this is used in the present analysis. The interface phase shift ϕ_i should vary by π across the Si band gap, and is given by

$$\text{Re} \left[-\cos^{-1} \left(2 \frac{E - E_L}{E_U - E_L} - 1 \right) \right] + \phi_0, \quad (2)$$

where Re refers to the real part, E is the energy, E_L is the lower edge of the Si band gap, E_U is the upper edge, and ϕ_0 is a constant [15,16]. The constant ϕ_0 is unknown and is the fitting parameter in a fit of the calculated binding energies of the quantum well states to the observed values. The calculated binding energies of the quantum well states for each quantum number n from the fit are shown as circles connected by lines in Fig. 1(b). The results agree well with the experimental values shown as crosses. The quantum well state at $N = 11$ is observed but is too close to the Fermi level for a determination of its position. The confinement edge at 0.5 eV is indicated by a horizontal dashed line in Fig. 1(b).

Annealing such atomically uniform films to increasingly higher temperatures results in roughening of the film, as has been seen in other systems [3,4,13]. This is evidenced by a sudden drop of the quantum well peak intensity, as shown in Fig. 2(a). Figure 2(b) shows the measured intensities for several N extracted from the spectra as a function of annealing temperature, which was increased at a rate of 1 K/min. The temperature at which each film begins to break up, the stability temperature, is extracted from the intersection of linear regressions of the data, as shown in Fig. 2(b). For even N values, the stability temperature is extracted by examining the behavior of a quantum well resonance or a quantum well state that is observable at an off-normal emission angle. The measured stability temperatures for various N are summarized in Fig. 3(a). Data points for the same N represent results from different samples, and the spread indicates the level of reproducibility.

Figure 3(a) shows that $N = 6$ and 8 are unusually stable compared to the other thicknesses, and a correlation with

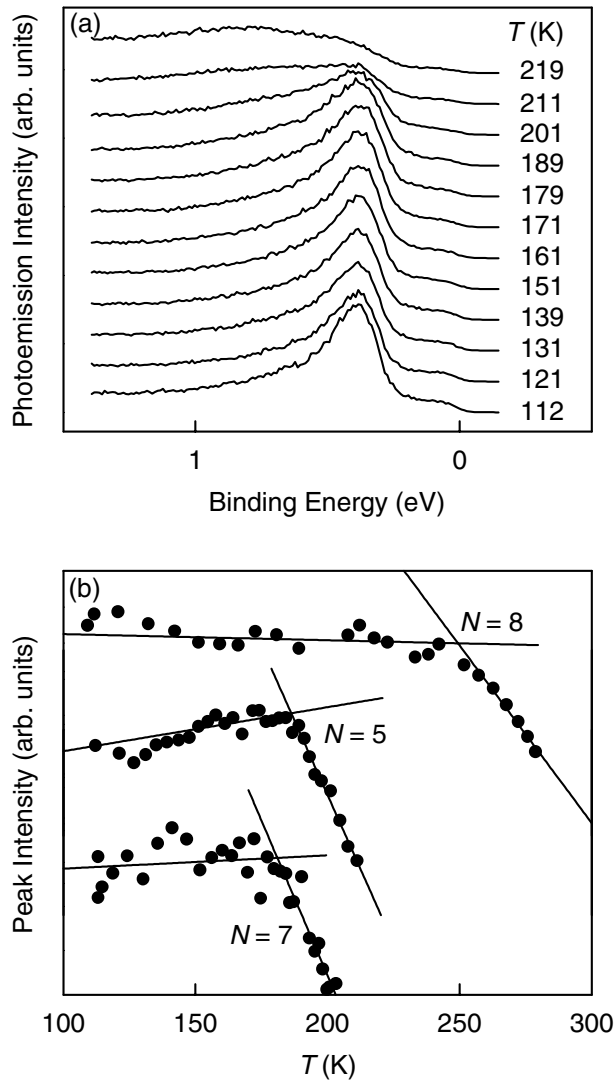


FIG. 2. (a) Photoemission spectra for a film thickness $N = 5$ at various annealing temperatures. (b) Intensities of quantum well peaks as a function of annealing temperature for $N = 5, 7,$ and 8 . The straight line segments are linear regressions of the data. Their interesting points indicate the temperatures at which the films become unstable.

the results in Fig. 1 is evident. Spectra from these thicknesses show no sharp quantum well peaks because in each case the first occupied state is below the confinement gap. Compared to the neighboring odd thicknesses $N = 5, 7,$ and 9 , where the first occupied state lies much closer to the Fermi level, the total electronic energy for $N = 6$ and 8 is expected to be lower. This implies, in turn, that $N = 6$ and 8 should be more stable, as observed experimentally. The above argument, while giving the right answer, is somewhat oversimplified. A more rigorous evaluation must involve a sum over all occupied states. An examination of Fig. 1(b) shows that, as N increases, each quantum well branch with a given n crosses the Fermi level and becomes occupied. A sharp change in the electronic density is expected at the crossing point and so are all

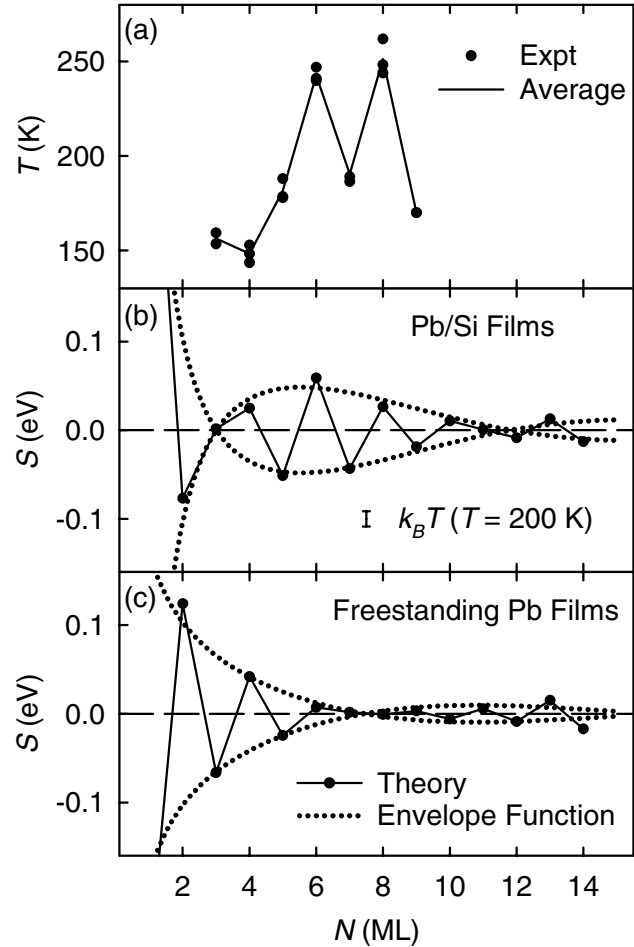


FIG. 3. (a) Annealing temperatures at which films of thicknesses N become unstable (dots). The averages are connected by line segments. (b) The S function, which determines stability, is plotted as a function of N . The circles, connected by line segments, are derived from a density functional calculation for Pb films on a compressed Si(111) substrate. The dotted curves represent envelope functions derived from a simple Friedel functional form. (c) is the same as (b) except that the films are freestanding. The magnitude of typical thermal energy $k_B T$ for $T = 200$ K is indicated.

physical properties of the film per density functional theory. The crossing points are evenly spaced at one-half of the Fermi wave length, or 2.2 ML. Thus, approximately bilayer oscillations are expected, explaining the apparent stability differences between even and odd values of N . However, 2.2 ML is not exactly 2 ML, and, over a sufficiently wide thickness range, the phase of the even-odd variations will be reversed by a beating effect [12,13].

Figure 3(b) shows the discrete second derivative of the surface energy per site $E(N)$,

$$S(N) = [E(N + 1) + E(N - 1)]/2 - E(N),$$

obtained by a density functional calculation for Pb on Si(111) [12,13]. If $E(N)$ is locally concave, S is negative, and the film is unstable against decay into islands or

terraces. Conversely, a large positive S implies a stable configuration. The figure shows that S oscillates with an approximately bilayer period, and the oscillations decay away at large N (bulk limit). The results can be well described by a Friedel-like functional form

$$\frac{\cos[2k_F(N + \Delta N)t]}{(N + \Delta N)^\alpha},$$

where k_F is the Fermi wavelength, t is the monolayer thickness, α is an exponent, and $\Delta N < 1$ is a correction term due to charge spillage at the film boundaries and is related to the boundary phase shift. The dotted curves in Fig. 3(b) are envelope functions derived from a fit using the Friedel form. Before proceeding, we need to mention that the lattices of Pb and Si are mismatched. To keep the numerical problem manageable, the calculation assumed a Si lattice constant equal to the Pb lattice constant. This altered interface condition could result in errors.

From the shape of the S function in Fig. 3(b), $N = 4, 6,$ and 8 should be more stable than the others, in agreement with the experiment except for the case $N = 4$. A possible reason for this discrepancy is inaccuracy in the interface condition for the calculation. Shown for comparison in Fig. 3(c) are the S function and its envelope functions for freestanding Pb films based on the same method of calculation. Bilayer oscillations are again present, but the envelope function appears very different due to a larger ΔN , corresponding to a more extended electron distribution for the freestanding films. This comparison illustrates a high sensitivity of the envelope function to the interface structure, which is difficult to model accurately. It is conceivable that a slight shift of the envelope function in Fig. 3(b) to the right can suppress the maximum at $N = 4$ and simultaneously enhance the maximum at $N = 8$, bringing conformity with the actual system. Yet another possible explanation is residual strain in the film, which is likely to be larger for thinner films and can cause thinner films to be less stable than predicted here. Clearly, further theoretical development in realistic calculations for lattice-mismatched systems is needed.

In summary, substantial variations in thermal stability for Pb films on Si(111) are observed and correlated with quantum oscillations in electronic structure between even and odd film thicknesses. A review of the underlying physics suggests similar Friedel-like even-odd oscillations for all other physical properties. Critical to the success of this experiment is the ability to prepare atomically uniform films. These are made in a two-step process—creating a Pb-terminated Si reconstruction followed by deposition at a low temperature. Silicon is the most important electronic material, but preparing smooth films is known to be difficult due to a high chemical reactivity of Si and lattice-mismatch-induced defects. The present results have interesting and significant implications for the science and technology of quantum devices.

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