The continued miniaturization of silicon-based electronic devices is pushing component layer thicknesses toward the nanoscale, and a critical hurdle along this path is atomistic fluctuation. An uncertainty in layer thickness or roughness at the monolayer level can lead to substantial and unacceptable property variations. The effect is generally on the order of $1/N$, where $N$ is the thickness of the film in terms of monolayers (ML). At the nanoscale, $1/N$ can be as large as 20%, and for a typical valence band width of $\sim 10$ eV, the resulting changes in the electronic structure can be severe or even catastrophic for device performance. Exact control of layer thickness and atomic uniformity is thus a critical issue, but so far has not been achieved for films grown on silicon. Yet this is extremely important in view of the vast technological and manufacturing base for the silicon industry. In this work, we show that Pb deposition on Si(111) at 100 K can lead to atomically uniform thin films provided that the Si substrate is pretreated appropriately. The resulting films support quantum well states [1-3] due to confinement of electrons in the Pb films by the band gap in the Si substrate. A measurement of such states by angle-resolved photoemission determines the film thickness and reveals a quantum electronic structure that varies substantially as the film thickness undergoes monolayer changes. The result is a rather dramatic contrast between films consisting of even and odd numbers of monolayers. These findings illustrate the importance of atomic layer precision for controlling the electronic structure of thin films.

Our angle-resolved photoemission measurements were performed at the Synchrotron Radiation Center, University of Wisconsin-Madison, using a Scienta analyzer equipped with a two-dimensional detector. The Si(111) substrates were prepared from commercial n-type wafers with a resistivity of 1-60 ohm-cm. The Pb films were prepared by sequential, incremental deposition at 100 K, and the photoemission spectra were taken with the sample at the same temperature. The three-dimensional color plot in Fig. 1 shows the normal-emission intensity as a function of Pb film thickness and binding energy relative to the Fermi level. Three major quantum well peaks are seen at thicknesses $N = 5, 7,$ and $9$. A weak resonance peak at higher binding energy is seen at $N = 8$.
the even layer thicknesses $N = 6$ and $8$ in the same energy range. These peaks represent quantum well states formed by confinement of the Pb $p$-band electrons by the Si band gap. No such quantum well states exist for $N = 6$ and $8$, as will be explained below.

The appearance of intense peaks for odd $N$ only has to do with 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 thus 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 [3]. One such weak resonance peak at a binding energy of 0.63 eV can be seen in the three-dimensional plot of Fig. 1 at $N = 8$. Further evidence for the confinement edge is seen in the line scan of the peak at $N = 5$ in Fig. 1. This peak, with a binding energy very close to the confinement edge, is asymmetric. Its higher-binding-energy side is substantially broader because this portion of the spectral weight lies outside the confinement range. 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 [4].

The binding energies of quantum well states are determined by the Bohr-Sommerfeld quantization rule [2, 3, 5]:

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

where $k$ is the wave vector, $t$ is the monolayer thickness, $\phi_s$ is the phase shift at the surface, $\phi_i$ is the phase shift at the interface, and $n$ is a quantum number. For a given $N$ and integer quantum numbers, this equation determines the allowed $k$ values, which in turn determine the binding energies of the quantum well states through the band dispersion relation $E(k)$. For Pb(111), the relevant band is the $p$ valence band with a known dispersion that extends from 4.2 eV below the Fermi level to 8.0 eV above the Fermi level [5]. The surface phase shift $\phi_s$ as a function of energy has been computed by a first-principles method [5], and this is used in the present analysis. The interface phase shift $\phi_i$ is given by

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

where $\text{Re}$ 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 $\phi_0$ is a constant [6, 7]. It is easy to verify that $\phi_i$ changes by $\pi$ across the Si band gap. The only unknown quantity in Eq. (1) is the constant $\phi_0$. This is treated as a fitting parameter in a fit of the

![Figure 2: Binding energies of quantum well states (circles connected by lines) deduced from a fit to the experimental results (crosses). The band structure of Pb and the phase shifts enter the model calculation. The only fitting parameter is an unknown constant offset in the interface phase shift. The quantum number $n$ for each branch is indicated.](image-url)
calculated binding energies of the quantum well states to the observed values. The calculated binding energies of the quantum well state from the fit are shown as open circles connected by lines in Fig. 2, and the quantum number $n$ for each branch is indicated. The results agree well with the experimental values shown as crosses. The experimental value for the quantum well state at $N = 11$ is not included in the figure because the peak is too close to the Fermi level for a precise determination of its position.

The confinement edge at 0.5 eV is indicated by a horizontal dashed line in Fig. 2. In agreement with experimental observations, no quantum well states exist, or only weak resonances are observed, for even $N = 4, 6, 8,$ and $10$, while intense quantum-well states are observed for odd $N = 5, 7,$ and $9$. This difference between even- and odd-$N$ configurations is just a consequence of the way that the quantum well states evolve as a function of thickness as seen in Fig. 2. This evolution is largely determined by the band structure [3, 5, 8, 9]. It happens that one half of the Fermi wave length in Pb is approximately two atomic layers, and a simple analysis based on Eq. (1) shows that a new quantum well state drops below the Fermi level for a film thickness increment of about two atomic layers [3, 5]. The corresponding changes in the occupied density of states should give rise to an oscillation period of about two atomic layers for essentially all physical properties of the films. Also in agreement with our experimental observation is that no quantum well states are predicted for $N = 1-3$.

Numerous groups have experimented with Pb growth on Si [8-13], but none has achieved atomic uniformity. Prior to this experiment, we had performed extensive experimentation with direct deposition on the (7x7) reconstructed Si(111) at various temperatures, but the resulting films were inevitably rough. In the present experiment, the atomic-layer uniformity is achieved by first preparing either the $\alpha$ or $\beta \left(\sqrt{3} \times \sqrt{3}\right)$ reconstructions [12, 14, 15]. Our experiment shows that deposition of Pb on the $\alpha$ phase, the $\beta$ phase, or any intermediate phases at a low temperature (100 K) leads to atomically uniform films. The final results are the same for the same total amounts of Pb deposition including the initial Pb coverages. The determination of film thicknesses is described in detail in [1].

The stability of the films has been measured, and some interesting features were observed, including the bilayer oscillation predicted by Wei et al. [17].

Why does Pb pretreatment promote uniform film formation, while direct deposition on Si(111)-(7x7) does not work? A possible explanation is that the (7x7) surface, with its complicated reconstruction involving adatoms, dimers, corner holes, and partial stacking fault, is not smooth on the atomic scale. These structural features can pin the Pb growth locally at low temperatures, resulting in small crystallites that are structurally incoherent. Increasing the substrate temperature to promote long-range diffusion and structural coherence leads to formation of islands instead of smooth films due to electronic effects [10, 16]. Pretreatment of Si by Pb leads to a smooth bulk-terminated Si substrate with a well-ordered Pb overlayer. This can be a good template for smooth growth upon further deposition at low temperatures. Our results illustrate an important issue in film growth – the initial surface structure can be a deciding factor for the morphological development of films. As shown in this study, proper conditioning of the starting surface allows us to make uniform films on Si, a result of potential interest and importance for nano and quantum electronics.

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