Theory of quantum size effects in thin Pb(111) films

C. M. Wei[1,2] and M. Y. Chou[2]

[1]*Institute of Physics, Academia Sinica, Nankang, Taipei, Taiwan 11529, Republic of China*
[2]*School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430*

We have carried out first-principles calculations of Pb (111) films up to 25 monolayers to study the oscillatory quantum size effects exhibited in the surface energy and work function. These oscillations are correlated with the thickness dependence of the energies of confined electrons, which can be properly modeled by an energy-dependent phase shift of the electronic wave function upon reflection at the interface. It is found that a quantitative description of these quantum size effects requires a full consideration of the crystal band structure.

An intriguing and unexpected feature has recently been discovered during epitaxial growth of metal thin films on semiconductors. Instead of forming three-dimensional islands of various sizes, as commonly observed for nonreactive interfaces, the metal atoms can arrange themselves into plateaus or islands of selective heights, with flat tops and steep edges under certain growth conditions. This unusual behavior was first observed in Ag/GaAs,[1] and later in a few other systems such as Ag/Si(111) (Ref. 2) and Pb/Si(111).[3–5] The implication could be significant, since the formation of these uniform, self-organized atomic structures points to a potentially interesting pathway to prepare functional nanostructures.

It is believed that this extra stability of metal films with specific thicknesses has an electronic origin[6] and can be explained by so-called quantum size effects due to electron confinement.[7] To better understand these phenomena, detailed experimental studies of island distribution, film morphology, and the electronic properties of these structures are needed. In this regard, attention has recently been focused on the growth of Pb islands/films on Si(111), to which various experimental surface-science techniques have been applied, including low-energy electron diffraction,[3,4] scanning tunnelling microscopy (STM),[4,5,8] and photoemission spectroscopy.[9] An interesting result found for this system is that islands of heights differing by bilayer increments are most abundant, even at low temperatures.[4] The spectroscopy of the quantized electronic states near the Fermi level has also been studied using STM,[5,8] which shows similar even-odd oscillations. These confined electrons can even be used to image the buried Si(111)-(7×7) superstructure under as much as 100 Å of Pb.[10] All of these experimental data were analyzed by a free-electron-like jellium model previously.

In order to provide a quantitative and unambiguous description of this interesting system, we present a first-principles calculation for the size-dependent properties of Pb thin films. As will be shown below, the actual band structure is needed to determine the periodicity of the oscillations of various physical properties as a function of thickness. In addition, the idea of using a phase shift of the electronic wave function upon reflection at the interface in the analysis and modeling of these phenomena[11] can be realistically tested by first-principles calculations. Since the in-plane lattice constant of the Pb (111) plane is 9% smaller than that of the

Si(111) substrate, the first monolayer of Pb deposited on Si(111) may have various configurations, and is spatially modulated by the substrate corrugation potential.[12] At higher coverage, flat-top islands of distinctive heights are formed upon the completion of the wetting layer(s) whose coverage and structure are still under debate. However, based on diffraction results the in-plane lattice constant for these islands is believed to be close to that of the bulk. Therefore, as a first-step investigation, we will study freestanding Pb films to understand the physical picture. The effect of the substrate will be discussed base on these results.

When the film thickness approaches the nanoscale, quantum confinement has a major impact on the system's physical properties. The itinerary electrons in metal films are confined in the z direction perpendicular to the film surface, resulting in discrete energy levels associated with so-called quantum-well (QW) states.[11] For s-p metals the energy dispersion in the xy direction remains nearly parabolic, giving rise to a series of energy subbands. As the film thickness D increases, these subbands sequentially cross the Fermi level. Because of this periodic crossing, the physical properties of the films would oscillate as D increases, as previously demonstrated by a jellium calculation.[7] For example, a local minimum (cusp) in the work function occurs every time a new QW state drops below the Fermi level and is occupied. The stability of the film could also be affected due to the variation in the electronic energy, which was previously discussed by using a square-well model.[6] If one goes beyond these simple models, one needs to take into account not only the fact that not only the thickness of the film is discrete, but also the crystal band-structure effect. Previous slab calculations for metal thin films[13–18] have confirmed the existence of a certain oscillatory behavior in the work function and surface energy. In this work we will cover an extended range of thickness and focus on a detailed analysis of the QW states and their correlation with the oscillation of various physical properties.

The calculations are carried out using the Vienna *ab initio* simulation package[19] based on density-functional theory with ultrasoft pseudopotentials[20] and plane waves, with the Pb d orbitals included as valence states. Periodic slabs separated by a vacuum region equal to 12 Pb layers are used. The Brillouin-zone summation is performed with a $20 \times 20 \times 1$ k-point grid, and the plane-wave energy cutoff is 144 eV.
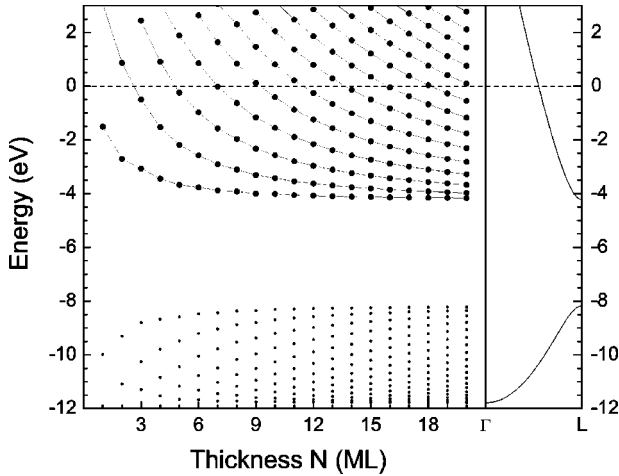
FIG. 1. Calculated energies of quantum-well states at $\bar{\Gamma}$ in Pb (111) thin films as a function of thickness, with the energy set to zero at the Fermi level. The results are obtained using the local-density approximation at the experimental lattice constant. The right panel shows the bulk energy dispersion in the [111] direction.
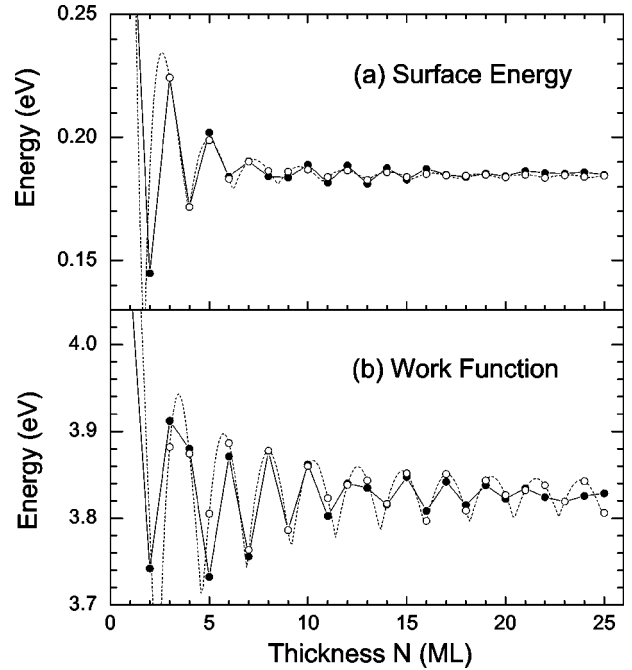

FIG. 2. (a) Surface energy per 1×1 unit cell and (b) work function of Pb (111) thin films as a function of thickness. The calculated results (solid circles) are obtained using the generalized gradient approximation at the theoretical lattice constant with layer spacings fully relaxed. The open circles and dashed lines represent the fitted values using Eq. (2) and with $\alpha = 2$ and 1 for the surface energy and work function, respectively.

Relativistic effects are included at the scalar level and the energy and force convergences are carefully checked. We have employed and tested both the local-density approximation (LDA) and the generalized gradient approximation (GGA).[21] The theoretical lattice constant for Pb in the GGA (LDA) calculation is 5.04 Å (4.88 Å), and 1.8% (1.4%) larger (smaller) than the experimental value of 4.95 Å.

Figure 1 shows the energies of the QW states at $\bar{\Gamma}$ as a function of the film thickness, calculated using the LDA at the experimental lattice constant without interlayer relaxations. The energy zero is set at the Fermi energy of each film. Changing the lattice constant to theoretical values will modify the bandwidth by a few tenths of eV, but the states near the Fermi level are hardly changed (no more than 0.1 eV). Interlayer relaxations are also studied at the theoretical lattice constant, and the corresponding energy change for the QW states near the Fermi level ranges from about 0.25 eV for the thinnest films to less than 0.1 eV for films thicker than ten atomic layers. However, the overall thickness-dependent variations of the QW state energies are similar in all different calculations mentioned above. Also plotted in Fig. 1 for comparison is the energy dispersion in the bulk along the [111] direction, which determines the energy range for the QW states. One can see that the s-p gap is about 4 eV, and that relevant QW states actually arise from the p band. If the energies of the QW states are grouped as indicated in Fig. 1, a branch moves down, crossing the Fermi level for every incremental increase in the film thickness of about 2.2 layers in the figure, which is consistent with the experimental finding of bilayer stability.

For s-p metals the QW energy levels are often described by the quantization condition

$$2k(\varepsilon)N\,d + 2\,\Phi(\varepsilon) = n2\pi, \tag{1}$$

where k is the corresponding wave vector for energy ϵ in the bulk band, N the number of layers, d the interlayer spacing

(2.86 Å), and n an integer starting from 0. Φ is an energy-dependent phase shift of the electronic wave function upon reflection at the film-vacuum interface, and is related to the logarithmic derivative of the wave function there. Using Eq. (1) one can calculate the periodicity for the QW states crossing the Fermi level, $\Delta N = \pi/(k_F d)$, where k_F is the Fermi wave vector. If we use the free-electron value of k_F for Pb, ΔN would be 0.7, which seems to be inconsistent with the curves in Fig. 1. This is due to the fact that in the real band structure of Pb, the s band is filled and the bottom of p band is at L. If we use the k_F value measured from L, which is 0.44 times π/d, the length of ΓL, ΔN, then becomes 2.2, in agreement with the pattern in Fig. 1. The branches indicated by solid lines in Fig. 1 are then characterized by quantum numbers $n = 0,1,2,\ldots$, with $n=0$ being the lowest branch, $n=1$ the next one, and so on.

The above analysis also suggests that oscillations exist in the size-dependent physical properties of the film. We have calculated both the surface energy and work function as functions of the film thickness. Shown in Fig. 2 are results from the GGA calculation for slabs with interlayer separations fully relaxed. The surface energy in Fig. 2(a) is defined as one-half of the energy difference between the film and the bulk with the same number of atoms, including the proper subtraction of a term linear in N.[22] If the thickness dependence is caused by the electronic structure, these results are expected to follow a simple oscillatory form multiplied by a damping factor. An approximately even-odd oscillation can clearly be seen in both the calculated surface energy and
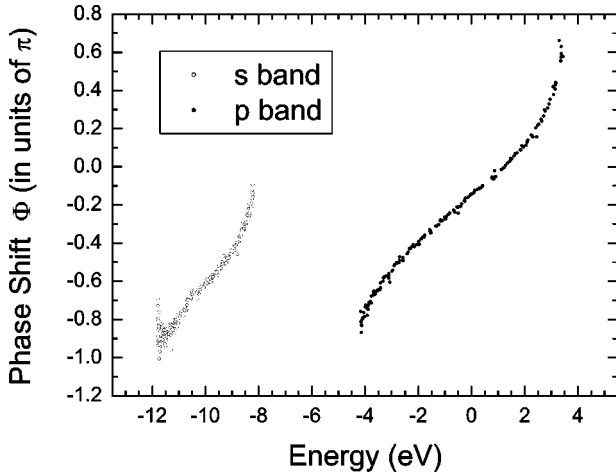
FIG. 3. The phase shift of the electronic wave function at the film-vacuum interface (see the text) as a function of the energy of quantum-well states in Pb(111) thin films.
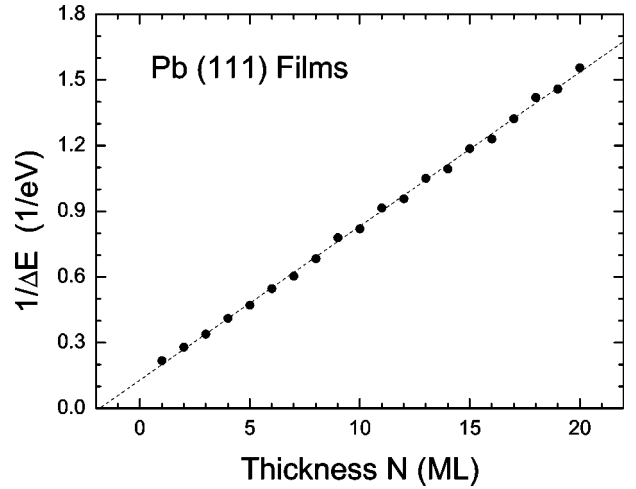

FIG. 4. The inverse of the energy spacing of quantum-well states near the Fermi level in Pb (111) thin films as a function of thickness. The dashed line is a linear fit to the calculated values.

work function [solid circles in Figs. 2(a) and 2(b), respectively]. This arises from the fact that the ratio $k_F d/\pi$ is very close to 1/2, the value producing a perfect even-odd oscillation. The film thickness with a low surface energy typically has a QW state deep below the Fermi level (see Fig. 1), consistent with the STM observations that the preferred heights of Pb islands on Si(111) (Ref. 4) and Cu(111) (Ref. 23) all had the last occupied QW state far from the Fermi level.

The calculated surface energy and work function as a function of N can be fitted by a damped sinusoidal function with periodic cusps to mimic the slope change at the filling of each subband. We used the following function to fit the results from $N=3$ to 25

$$\frac{A|\sin(k_F d N + \varphi_0)| + B}{N^\alpha} + C \tag{2}$$

where A, B, C, α, and φ_0 are N-independent constants, and k_F is measured from L. The fitted results are shown by open circles and dashed lines in Fig. 2. α is found to be around 2 for the surface energy, as expected from the decay pattern of the energy separation of the QW states as N increases. For the work function α is very close to 1 in the fit.[24] Overall, Eq. (2) represents the oscillatory data quite well and the oscillations are similar for the GGA and LDA results.[25]

Equation (1) has been successfully used to model QW states in metal overlayers on a metal substrate, and to obtain the bulk band structure by photoemission from these QW states.[11] However, its validity has never be rigorously tested by full-scale first-principles calculations. From each of the QW state energies in Fig. 1, one can extract the phase shift $\Phi(\varepsilon)$ at that energy by using Eq. (1) and the value of k (measured from L in the case of the p band) deduced from the calculated bulk band structure. The results are plotted in Fig. 3, with data points obtained from the QW states in the films of various thickness. For our choice of quantum number n in Eq. (1), Φ starts from about $-\pi$ at the bottom of both the s and p bands. The total phase shift variation for the

filled s band is close to π. The fact that the data points follow the s and p curves with little scattering indicates that Eq. (1) is indeed a good description for states below the vacuum level.

The QW states near the Fermi level are accessible by STM measurements. Equation (1) can also give the approximate level spacing ΔE between the last occupied state and the first unoccupied state. Taking the derivative of Eq. (1) with respect to energy and evaluating it at the Fermi level for a given N, we have

$$\frac{1}{\Delta E} \approx \frac{2d}{h v_F} N + \frac{1}{2\pi} \Phi'(\varepsilon_F), \tag{3}$$

where v_F is the Fermi velocity obtained from the slope of the band at the Fermi level, and $\Phi'(\varepsilon_F)$ the energy derivative of the interface electronic phase shift at the Fermi level. Therefore, the measured $1/\Delta E$ curve should be a linear function of N. The slope is connected to v_F and the intersect gives $\Phi'(\varepsilon_F)$. Figure 4 shows the calculated result for freestanding Pb films using energies in Fig. 1. The fact that the points closely following a straight line indicates that Eq. (3) is largely satisfied. Note that the intersect of the linear curve with the horizontal axis is not at $N=0$, due to the nonzero energy derivative of Φ at the Fermi level.

Based on the above findings, it would be possible to understand how the substrate quantitatively affects these results. If the electronic confinement is still present, the film-substrate interface would provide a different boundary condition, and therefore a different phase shift for the electronic wave function than that at the film-vacuum interface. Hence $\Phi(\varepsilon)$ in Eq. (1) and $\Phi'(\varepsilon_F)$ in Eq. (3) should be replaced by the average of the two contributions. From Eq. (1) the energies of the QW states would be changed for a given N, but the periodicity in N for the QW states dropping below the Fermi level stays the same. Therefore, all size-dependent physical properties such as the surface energy and work function would show oscillations similar to those in Fig. 2, but may have a different value of φ_0 in Eq. (2). In

other words, the overall even-odd oscillations should still be present. In addition, the slope of the linear curve in Fig. 4 would be the same, but the curve for the film on a substrate would be shifted horizontally, indicating a different energy derivative for the phase shift at the Fermi level. For Pb/Si(111) the intersection with the horizontal axis has been found to be around -3 experimentally,[5] shifted toward the left from the present calculated value of about -1.8 for free-standing films.

In summary, we have studied the quantum size effect in Pb (111) films up to 25 ML by first-principles calculations. The thickness dependence of the energies of confined electrons relative to the Fermi level is found to be responsible for the variations in the physical properties of the film. An energy-dependent phase shift for the electronic wave function at the interface turns out to be a useful quantity in ana-lyzing these quantum-well state energies. The oscillations in the surface energy and work function as a function of thickness can be described by a damped sinusoidal function with the periodicity determined by an appropriate choice of the Fermi wave vector. We would like to thank Professors T.-C. Chiang, H. H. Weitering, and M. C. Tringides for helpful discussions.

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[1] A.R. Smith, K.-J. Chao, Q. Niu, and C.K. Shih, Science **273**, 226 (1996).

[2] L. Gavioli, K.R. Kimberlin, M.C. Tringides, J.F. Wendelken, and Z. Zhang, Phys. Rev. Lett. **82**, 129 (1999).

[3] K. Budde, E. Abram, V. Yeh, and M.C. Tringides, Phys. Rev. B **61**, R10602 (2000); V. Yeh, L. Berbil-Bautista, C.Z. Wang, K.M. Ho, and M.C. Tringides, Phys. Rev. Lett. **85**, 5158 (2000).

[4] M. Hupalo, S. Kremmer, V. Yeh, L. Berbil-Bautista, and M.C. Tringides, Surf. Sci. **493**, 526 (2001); M. Hupalo and M. C. Tringides, Phys. Rev. B **65**, 115406 (2002).

[5] W.B. Su, S.H. Chang, W.B. Jian, C.S. Chang, L.J. Chen, and T.T. Tsong, Phys. Rev. Lett. **86**, 5116 (2001).

[6] Z. Zhang, Q. Niu, and C.K. Shih, Phys. Rev. Lett. **80**, 5381 (1998).

[7] F.K. Schulte, Surf. Sci. **55**, 427 (1976).

[8] I.B. Altfeder, K.A. Matveev, and D.M. Chen, Phys. Rev. Lett. **78**, 2815 (1997).

[9] A. Mans, H. Dil, A. Ettema, and H. H. Weitering (unpublished).

[10] I.B. Altfeder, D.M. Chen, and K.A. Matveev, Phys. Rev. Lett. **80**, 4895 (1998); I.B. Altfeder, V. Narayanamurti, and D.M. Chen, *ibid.* **88**, 206801 (2002).

[11] For a review, see T.-C. Chiang, Surf. Sci. Rep. **39**, 181 (2000).

[12] H.H. Weitering, D.R. Heslinga, and T. Hibma, Phys. Rev. B **45**, 5991 (1992).

[13] P.J. Feibelman, Phys. Rev. B **27**, 1991 (1983); P.J. Feibelman and D.R. Hamann, *ibid.* **29**, 6463 (1984).

[14] P.J. Feibelman, Phys. Rev. B **65**, 129902(E) (2002).

[15] S. Ciraci and I.P. Batra, Phys. Rev. B **33**, 4294 (1986); I.P. Batra, S. Ciraci, G.P. Srivastava, J.S. Nelson, and C.Y. Fong, *ibid.* **34**, 8246 (1986).

[16] K.F. Wojciechowski and H. Bogdanów, Surf. Sci. **397**, 53 (1998), and references therein for Li films.

[17] A. Kiejna, J. Peisert, and P. Scharoch, Surf. Sci. **432**, 54 (1999), and references therein for Al films.

[18] G. Materzanini, P. Saalfrank, and P.J.D. Lindan, Phys. Rev. B **63**, 235405 (2001); P. Saalfrank, Surf. Sci. **274**, 449 (1992).

[19] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996) and references therein.

[20] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[21] J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).

[22] J.C. Boettger, J.R. Smith, U. Birkenheuer, N. Rösch, S.B. Trickey, J.R. Sabin, and S.P. Apell, J. Phys.: Condens. Matter **10**, 893 (1998), and references therein.

[23] R. Otero, A. L. Vázques de Parga, and R. Miranda, Phys. Rev. B **66**, 115401 (2002).

[24] F.K. Schulte, Phys. Status Solidi B **79**, 149 (1977).

[25] The large-N limit of the surface energy is 0.18 eV using the GGA, consistent with the previous theoretical estimate in Ref. 14, but is significantly smaller than the experimental value of about 0.37 eV. The LDA gives a better value of 0.25 eV per surface atom. For the work function, the GGA and LDA give large-N limits of 3.8 and 4.0 eV, respectively, in good agreement with the experimental value of 4.05 eV.