Quantum size effect in Pb(100) films: Role of symmetry and implications for film growth

Dengke Yu,[1] Matthias Scheffler,[1] and Mats Persson[1,2]
[1]*Theory Department, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195, Berlin-Dahlem, Germany*
[2]*Department of Applied Physics, Chalmers University of Technology, SE-412 96, Göteborg, Sweden*
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We show from density-functional calculations that Pb(100) thin films exhibit quantum size effect with a bilayer periodicity in film energies, film relaxations, and work functions, which originate from different symmetry of the stacking geometry of odd and even layer films. This symmetry-driven quantum size effect on the film energy could allow for growth of "magically" thick even-layer Pb(100) films on an appropriate substrate. Furthermore, it is found that the quantum well states in a simple metal film can be classified into σ-bonded and π-bonded states, which quantize independently.

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The so-called "electronic growth" model of metallic thin film on a semiconductor substrate has attracted much scientific and technological interest.[1] This model provides conditions for the growth of atomically flat thin films or nanostructures, which are of significant technological interest. The underlying physical mechanism behind "electronic growth" is the quantum size effect (QSE) on the film energy introduced by quantum well (QW) states in the film. In addition to the film energy, the energy gain associated by the charge transfer occurring at the film semiconductor interface needs also to be considered to determine the film stability. The total energy of the system may then result in "critical" thicknesses in which the film is stable when the number of atomic layers is above or below a critical number and "magical" film thicknesses in which the film has a pronounced stability for a certain number of atomic layers. The "electronic growth" model has been very successful in understanding observed "critical" thicknesses of alkali metal and noble metal overlayers grown on a GaAs surface,[1] and the observed "magical" thicknesses of Pb(111) films or islands on various substrates.[2–6]

The nature of observed QW states and the associated QSE in metal film have so far been well-understood from simple models based on bulk band structure and Fermi surface nesting.[7–10] In general, QW states are formed by the quantization of the valence electrons confined in the perpendicular direction of the thin film, as described by the phase accumulation model. The energies of the QW states are then obtained from the energies of the valence bulk bands at the quantized wave vectors. This simple model has been widely used in analysis of photoemission measurements of QW states.[8–10] The QSE on the film energy and other physical properties arises from the consecutive occupation of QW states with increasing film thickness. An enhanced density of states at the Fermi surface by QW states is then obtained from extremal spanning (nesting) vectors $\mathbf{q}$ of the Fermi surface that are perpendicular to the film, resulting in a QSE period $\lambda_{QSE}=2\pi/q$ for the film energy. For a free-electron model of the bulk bands, corresponding to a spherical Fermi surface, $q=2k_F$ where k_F is the Fermi wave vector and $\lambda_{QSE}=\pi/k_F$.

This simple model for QSE has been supported by first-principles, electronic structure calculations for various systems. Schulte[11] found that the electron densities, potentials, and work functions of a thin jellium film exhibited QSE with a period π/k_F in accordance with a free-electron model. Feibelman[12] and Batra *et al.*[13] found a QSE in the surface energy and surface relaxation of both A1(111) and Mg(0001) thin films. Wei and Chou[14] found that the QSE period for surface energies and work functions of thin Pb(111) films was consistent with a spanning vector in the Pb bulk band structure in the [111] direction. The observed oscillations of film thickness and interlayer spacing had the same QSE period.[3,6,15–17] So far the calculated and observed QSE periods can be simply understood from a nesting vector of the bulk band structure along the direction perpendicular to the film, which projects to the center of the film Brillouin zone (FBZ).

In this Brief Report we show from a density-functional theory (DFT) study of thin Pb(100) films that the symmetry of the stacking geometry of a thin film can have a profound influence on the QSE through QW states at the FBZ boundary. In particular, the film energy, relaxations, and work functions exhibit a bilayer periodicity that cannot be understood in terms of nesting vectors of the Fermi surface along the ΓX direction in the bulk BZ. This symmetry effect is a general phenomena for fcc(100) [and bcc(100)] films but should only be important for the film energy when the material also has a large band gap around the Fermi level at the FBZ boundary.

We have carried out DFT calculations of the total energy, geometric and electronic structure of freestanding Pb(100) films using a pseudopotential, plane-wave basis method within the local-density approximation. Technical details can be found in Ref. 18. Spin-orbit coupling was not considered.

As shown in Fig. 1, the calculated film energies and relaxations of the freestanding, thin Pb(100) films exhibit pronounced QSE. All these quantities exhibit a characteristic damped odd-even-layer alternation. The film energies of the relaxed films have a much more pronounced bilayer oscillation than the bulk truncated film, showing that the QSE on the relaxations contribute to the oscillations of the film energy in a cooperative manner. Both the film thickness and the first interlayer spacing show very similar oscillatory behavior. Also the work functions of the relaxed films (not shown here) exhibit QSE and oscillate in an antiphase manner relative to the oscillations of the film energy (i.e., work function maxima appear at the film energy minima).

A key issue is to understand why the QSE in thin Pb(100)

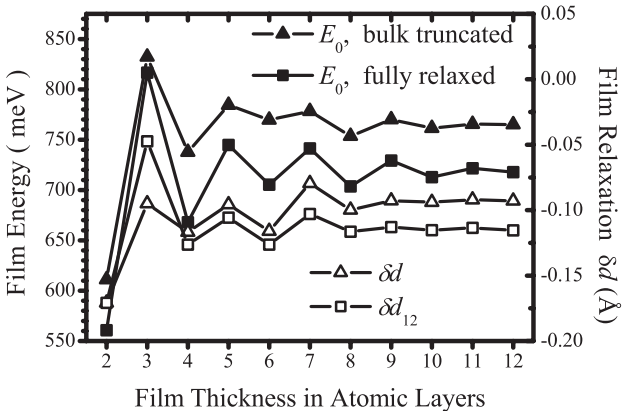

FIG. 1. Film energy E_0 per unit cell (left axis) and geometrical relaxations δd and δd_{12} (right axis) of freestanding Pb(100) films with respect to the number of atomic layers. E_0 of both the bulk truncated and the fully relaxed film are shown. E_0 is obtained by subtracting the bulk contribution from the total energy of the film per unit cell. δd and δd_{12} are the changes of the total film thickness and the first interlayer spacing from their truncated bulk values, respectively. Note that the energy and the relaxations exhibit a characteristic odd-even-layer alternation.

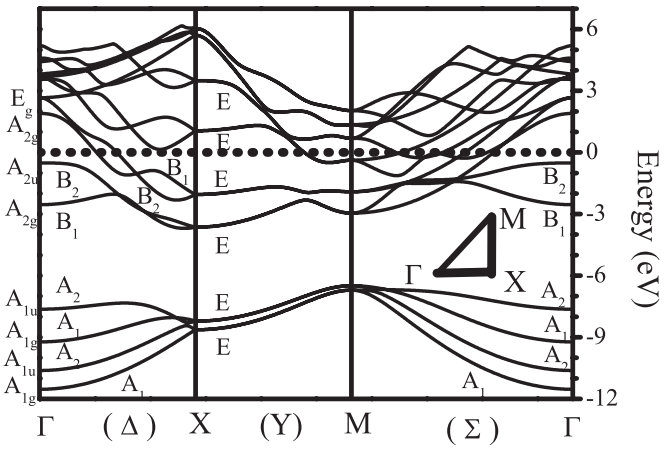

FIG. 2. Band structure of a four-layer, freestanding Pb(100) film along high symmetry directions in the film Brillouin zone (FBZ). These directions are depicted in the irreducible part of the FBZ. The symmetry characters of the various states at the Γ point and along the symmetry lines in the FBZ are indicated. Note that the states along the Y line are twofold degenerate in an even-layer film, and are nondegenerate in an odd-layer film. Fermi energy is set to 0 eV.

films has a bilayer period. We first show that this periodicity cannot simply be understood in terms of nesting vectors of the Fermi surface along the ΓX direction. The band structure around the Fermi level is dominated by bands derived from atomic p orbitals. Along the ΓX direction, corresponding to the perpendicular direction of the film, the Fermi surface has a nesting vector $q=1.36\pi/a$ corresponding to $\lambda_{QSE}=2.9d_{100}$ where d_{100} is the interlayer spacing. Thus a QSE period of about three (100) layers is expected in contrast to the calculated bilayer period for the QSE.

As a first step to understand the calculated QSE period, we have studied the QW states of the isolated 2–12 layer thick Pb(100) films. In Fig. 2 we show, as an illustrative example, the band structure of a bulk-truncated, four-layer Pb(100) film in the irreducible part of the film Brillouin zone (FBZ). The symmetry characters of the bands are indicated. For each wave vector in the FBZ, the discrete set of bands corresponds to QW states. Note that the bulk s and p subbands are separated by a gap of about 4 eV. The number of QW (s-QW) states derived from the bulk s bands is given by the number of layers (N) in the film, whereas there are $3N$ p-QW states derived from the bulk p bands. Only p-QW states cross the Fermi level and are relevant for the QSE. The p-QW states disperse either to higher energy or lower energy away from the Γ point depending on their orbital character being $p_z(\sigma)$- or $p_{x,y}(\pi)$-like. These states exhibit many "avoided crossings" accompanied with interchange of their characters. A key observation about QW states of these films that cannot be understood from the bulk band structure is the lifting by odd-layer films of the twofold degeneracy of QW states along the Y symmetry axis in even-layer films. Note that the projected bulk band structure on this axis is twofold degenerate.

To understand the effect of the odd-even layer alternation of the degeneracy on the consecutive filling of the QW states, we show in Fig. 3 the calculated layer dependence of the energy spectra of p-QW states at high symmetry points in the FBZ. The p-QW states of π bonding character at Γ and X points and p-QW states of σ bonding character at the M point do not cross the Fermi level and are accordingly not shown.[19] The occupied bands at Γ cannot accommodate all the p-electrons. In principle, it is necessary to consider the QW states at the whole FBZ, in particular at all the high symmetry points.

Only the QW states at the X point have a bilayer periodicity in Fig. 3. It is clear that the QW states at the Γ point cross the Fermi level by a period of about three layers in good agreement with the perpendicular spanning vector in the ΓX direction. Note that at the M point, the twofold degeneracy of the π-like QW states are not lifted by odd-layer films. However, at the X point (and along Y symmetry axis) this degeneracy is lifted by odd-layer films corresponding to a bilayer periodicity. In particular for states crossing the Fermi level, the splitting is anomaly large because of a large gap of about 1.5 eV in the projected bulk p band structure along the Y symmetry axis. The zone boundary band gap in the thin film therefore exhibits an odd-even-layer oscillation, similar to that found in Si(100) thin films.[20]

In general, QW states from different regions of the FBZ all contribute to the film total energy. In particular, the QSE period will be determined from the extremal perpendicular spanning (nesting) vectors which determine the period of the enhanced DOS at Fermi level. In the case that QW states at zone center dominate, the free-electron-like model is able to give reasonable prediction of the film stability, e.g., Pb(111) film,[14] Ag(100) film.[21] In the case of the Pb(100) thin film, the QW states at BZ boundary give rise to the periodicity of the film energy.

The different degeneracies along the FBZ boundary in odd and even layer Pb(100) films is due to the symmetry of the layer stacking. Because the Pb(100) film [and the (100)

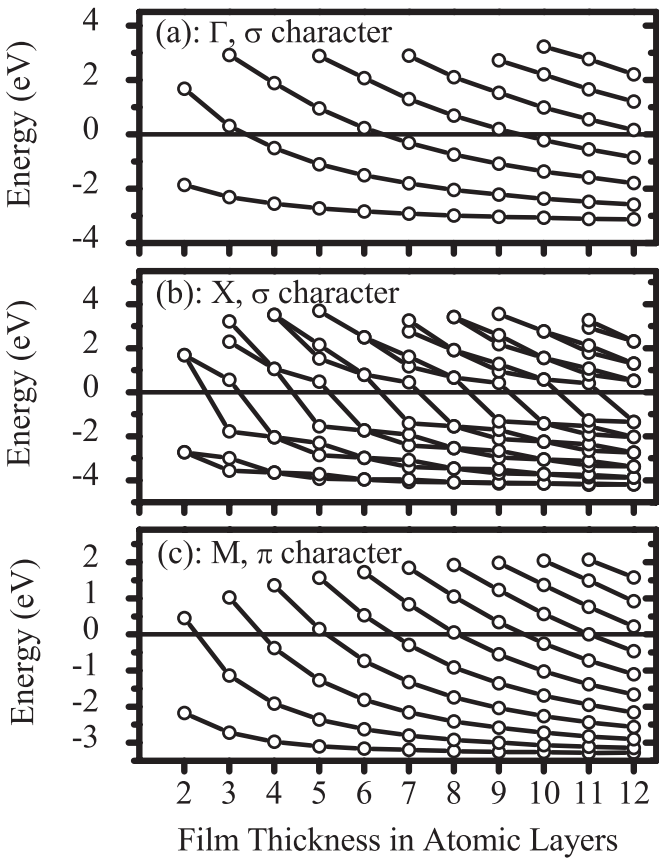

FIG. 3. Energy spectra of quantum well states derived from bulk p bands at the high symmetry points Γ, X, and M in the film Brillouin zone as a function of the number of atomic layers in the film. At the Γ and X points only states with σ bonding character are shown, whereas at the M point only states with π bonding character are shown. The states with different bonding characters at these $\mathbf{k}$ points do not cross the Fermi level and are not shown. Note that the splitting of the states around the Fermi level in panel (b) exhibit an odd-even-layer alternation. The Fermi energy is set to 0 eV.

film of any fcc or bcc metal] has an ABAB…stacking sequence, odd- and even-layer films have different symmetry. An odd-layer film has an mirror plane on the central layer. The point group is D_{4h}, and the space group is symmorphic. For an even-layer film, there is no such direct mirror plane but a glide plane. The resulting space-group D_{4h}^7 is nonsymmorphic. For the odd-layer film, the point group along the Y axis is C_{2v}, and the bands of odd-layer film are always nondegenerate along Y. For the even-layer films, nonprimitive translations are involved along this axis and a multiplier representation has to be considered (see, e.g., Ref. 22). Only a single two-dimensional representation is found and the bands in even-layer films are all twofold degenerate along the Y axis.

So far observed and calculated QW states of thin metal films have been successfully described by the bulk band structure and the phase accumulation model. However, as illustrated by the results for the QW states of thin Pb(100) films, the energies of the QW states at the FBZ boundary of (100) film of any fcc (or bcc) metal are determined not only by the film thickness, but also by the symmetry of the layer stacking geometry. A mirror plane for odd-layer film and a glide plane for even-layer film result in nondegenerate and twofold degenerate QW states along the Y axis. This symmetry effect cannot simply be captured by the bulk band structure and the phase accumulation model. However, the size of the splitting across the Fermi level determining the QSE in film energy and relaxation is material specific because it depends on the presence of a large band gap at the Fermi level at the boundary of FBZ. For instance, in the case of a Al(100) film, we have a similar symmetry effect but this band gap is well above Fermi-level and the film energy QSE period is given by the free electron result.

It is a challenge to find a substrate which supports the growth of Pb(100) films and where the symmetry-driven QSE survive. Among semiconductor surfaces there is no obvious candidate that is commensurate with the Pb(100) film. These surfaces tend to favor the growth of close packed Pb(111) films. An interesting class of substrates for the growth of (100) metal films that have favorable lattice matching are provided by the oxides of the alkaline-earth metals. The wide band gap of these metal oxides favors also confinement of the QW states within the film. For instance, pseudomorphic growth of Ag(100) films has been observed on a MgO(100) surface.[23,24] Furthermore, a DFT calculational study of this system showed that these films should exhibit QSE of the film energy from QW states in the film.[25] In the case of Pb, we have also a relatively small lattice mismatch of about 3% for the (100) films on the BaO(100) and SrO(100) surfaces that should favor pseudomorphic growth of Pb(100) films on these surfaces. Thus these two surfaces could be candidates for the observation of a symmetry-driven QSE in the growth of Pb(100) films.

Finally, we would like to discuss the nature of the quantization of the QW states as obtained from a scrutiny of their wave functions (WF). It is found that the σ- and the π-like QW states form two independent series of states.[19] As expected, the lowest QW state derived from the bulk s-band has zero nodes, while the second one has one node, etc. The bulk s-band accommodates 20 QW states for a 20 layer film with a maximum of 19 nodes. The low-lying p_z-QW states have σ character. The lowest p_z-QW state has 20 nodes and constitutes the next state in the σ series, followed by the p_z-QW states having 21, 22, 23, 24 nodes, etc. The higher-lying $p_{x,y}$-QW states with π character are twofold degenerate and form an independent series of QW states from the σ series of s- and p_z-QW states. The lowest-lying π state (E_g) has quantum number one (zero nodes), the second π level (E_u) has quantum number two (one node), etc. The separate quantizations of σ and π states are rather general. We have investigated the QW states in linear, isolated chains of Na, Mg, Al, and Pb. The QW states spectra in these linear chains are quite similar to that of the Pb(100) film at the Γ point. The twofold degenerate π states are higher in energy and quantize independently from the σ states.

In summary, we have shown from density functional calculations that Pb(100) thin films exhibit quantum size effect with an odd-even-layer alternation of film energies, film relaxations, etc., which are due to the different symmetry of the stacking geometry in odd and even layer Pb(100) thin films. The quantum well states at the film Brillouin zone

boundary have a twofold degeneracy in even-layer films, which are lifted in odd-layer films. Furthermore, a large band gap at the Brillouin zone boundary in Pb(100) films makes the odd-even alternation of the splitting of the bands embracing the Fermi level significant for the film energy. This symmetry-driven quantum size effect suggests that a Pb(100) film with an even number of layers supported by an appropriate substrate [e.g., BaO(100) or SrO(100)] may show up as "magic thicknesses." Furthermore, we show that the quantum well states in a simple-metal film can be classified into σ and π bonded states in the perpendicular direction of the film, which quantize independently.

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