Quantum size effect in Pb(100) films: the role of symmetry and implication for film growth

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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. The bilayer periodicity of the film energy is argued to survive on a semiconductor substrate, which should allow the growth of "magically" thick even-layer Pb(100) films. Furthermore, it is found that the quantum well states in a simple metal film can be classified into $\sigma$-bonded and $\pi$-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\textsuperscript{[1,3,4]}. This model provides conditions for the growth of atomically-flat thin films or nano-structures, 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 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\textsuperscript{[1]} and the observed "magical" thicknesses of Pb(111) films or islands on various substrates\textsuperscript{[2,8,9,10]}.

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\textsuperscript{[2,3,4,5,6,7,8,9,10,11,12,13,14,15]}. 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\textsuperscript{[9,10,11,12,13]}. 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 $q$ of the Fermi surface that are perpendicular to the film, resulting in 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\textsuperscript{[10]} found that the electron densities, potentials, and work functions of a thin jellium film exhibited QSE with a period $\pi/k_F$ in accordance with a free-electron model. Feibelman\textsuperscript{[11]} and Batra et al.\textsuperscript{[12]} found a QSE in the surface energy and surface relaxation of both Al(111) and Mg(0001) thin films. Wei and Chou\textsuperscript{[13]} 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 [111] direction. The observed oscillations of film thickness and interlayer spacing had the same QSE period\textsuperscript{[2,8,9,10,12,13,14,15,16,11,10]}. 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 letter 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 FX 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 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.\textsuperscript{[17]}. Spin-orbit coupling...
metrical relaxations shown. From the total energy of the film per unit cell. Pb(100) films with respect to the number of atomic layers. 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.

was not considered.

As shown in Fig. 1, the calculated film energies and relaxations of the free-standing, 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 anti-phase 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) 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 inter-layer 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 to 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 $p_x$- ($\sigma$-) 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 two-fold degeneracy of QW states along the $Y$ symmetry axis in even-layer films. Note that the projected bulk band structure on this axis is two-fold 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 $\pi$ bonding character at Γ and X points and $p$-QW states of $\sigma$ bonding character at the M point do not cross the Fermi level and are accordingly not shown [18]. 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.
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 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.

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 3 layers in good agreement with the perpendicular spanning vector in the ΓX direction. Note that at the M point, the two-fold 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 [10].

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 case that QW states at zone center dominate, free-electron-like model is able to give reasonable prediction of the film stability, e.g., Pb(111) film [13], 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) 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 $D_{4h}$ is non-symmorphic. For the odd-layer film, the point group along Y axis is $C_{2v}$, and the bands of odd-layer film are always non-degenerate along Y. For the even-layer films, non-primitive translations are involved along this axis and a multiplier representation has to be considered (see e.g., Ref. [21]). Only a single two-dimensional representation is found and the bands in even-layer films are all two-fold degenerate along the Y axis.

So far the observed and calculated QW states of thin metal films has 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 non-degenerate and two-fold degenerate QW states along Y axis. This symmetry effect can not simply be captured by the bulk band structure and the phase accumulation model. However, the size of the splitting across the Fermi level and 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.

An important remaining issue is whether the bilayer periodicity of the freestanding Pb(100) film energy survives on adsorption on a semiconductor. A simple estimate of the energy of a thin Pb(100) film grown on a semiconductor surface using the “electronic growth” model [11] indicates that the bilayer periodicity survives. In this model, the total energy $E_t$ of a metal film grown on a semiconductor substrate is given by $E_t = E_0 - E_c$, where $E_0$ is the (relaxed) film energy shown in Fig.1 and $E_c$ is the energy gain per surface unit cell due to charge transfer at the metal semiconductor interface. This energy gain can be estimated in a simple capacitor model: $E_c = C(\Delta \Phi)^2$ [11, 22], where $C$ is a phenomenological pa-
rameter specific to the interface and $\Delta \Phi$ is the difference between the work functions of the clean substrate and the film. For example, $E_c$ can be estimated in the case of Si(111)-(7 × 7) semiconductor substrate by using the same value for $C = 0.033/(eV \AA^2)$ as used by Yeh et al. for similar Pb(111) films (similar charge density, work function, surface energy, etc.), and using the measured value 4.75 eV for the substrate $\Phi$. Our calculated values for the film $\Phi$. Using this estimate for $E_c$ and the calculated values for $E_0$, the resulting values for $E_t$ are 0.47, 0.65, 0.54, 0.57, 0.54, 0.59, 0.54 eV for 2, 3, 4, 5, 6, 7 and 8 layers of the Pb(100) film. Because the oscillations of the work functions are in antiphase relative to those of $E_0$, $E_c$ partly compensates the strong oscillation of $E_0$ but its odd-even layer alternation has not been destroyed.

The above analysis does not necessarily suggest that Pb(100) films can grow on Si(111)-(7 × 7). But it does illustrate that the total energy can have an odd-even oscillation when a Pb(100) thin film is grown on a semiconductor substrate. However, one has to choose a substrate with a good lattice match so that the elastic energy is negligible. The Pb(100) film should then exhibit “electronic growth” if care is taken to relieve possible kinetic limitations.

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 $\sigma$- and the $\pi$-like QW states form two independent series of states. 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 $\sigma$ character. The lowest $p_z$-QW state has 20 nodes and constitutes the next state in the $\sigma$ series, followed by the $p_z$-QW states having 21, 22, 23, 24 nodes, etc. The higher-lying $p_x, y$-QW states with $\pi$ character are two-fold degenerate and form an independent series of QW states from the $\sigma$ series of $s$- and $p_z$-QW states. The lowest-lying $\pi$ state ($E_\pi$) has quantum number one (zero nodes), the second $\pi$ level ($E_{\pi}$) has quantum number two (one node), etc. The separate quantizations of $\sigma$ and $\pi$ 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 $\Gamma$ point. The two-fold degenerate $\pi$ states are higher in energy and quantize independently from the $\sigma$ 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 two-fold 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 alternation of the film energy is argued to survive on a semiconductor substrate. Even-layer Pb(100) films should be especially stable and may show up as “magic thickness”. Furthermore, we show that the quantum well states in a simple-metal film can be classified into $\sigma$ and $\pi$ bonded states in the perpendicular direction of the film, which quantize independently.

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