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Quantum size effects in Pb films from first principles: The role of the substrate

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Three different Pb films—free standing, on a semiconducting Ge(111) substrate, and on a metallic Cu(111) substrate—are studied with first-principles calculations. Our studies show that the properties of these films—surface energy, work function, and lattice relaxation—oscillate strongly with the film thickness. The oscillation follows a bilayer pattern interrupted by even-odd crossovers. However, the positions of the crossovers and the separation between the crossovers depend on the substrate, showing that the substrate plays an important role in the Pb film properties. In particular, the results for Pb films on Cu(111) substrate challenge the existing physical picture of Pb films.

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I. INTRODUCTION

One of the key issues in nanoscience or nanotechnology is to control the material size at nanoscales to achieve desired functionalities with quantum engineering. Recent experimental developments in the epitaxial growth of metallic thin films have offered such a possibility. It has been found that some metals can form atomically flat continuous films or large islands with atomically flat tops with selective heights.[1] More importantly, one has found that the properties of these films depend strongly on the film thickness, such as superconducting T_c (Refs. 2 and 3) and electron-phonon coupling.[4] This means that one is allowed to control the film thickness at the atomic scale for desired film properties. These epitaxial systems include Ag/GaAs(110),[5] Ag/Si(111),[6] Ag/Fe(100),[7] Pb/Si(111),[8–18] Pb/Cu(111),[19] Pb/Ge(100),[20] and, most recently, Pb/Ge(111).[21]

This interesting phenomenon is commonly attributed to the quantum size effect[22,23] (QSE): Due to the small dimension perpendicular to the metallic film and the confinement of interfaces, the electronic energy bands are discretized and form quantum-well states[24–27] (see Fig. 1). The discretization can lead to the oscillatory dependence of the film's total energy on its thickness, instead of the linear dependence on thickness for very thick films. This oscillatory behavior implies that a thin film of certain layers may be energetically favored than other layers, leading to the formation of an atomically flat film.

In comparison with other films, the Pb(111) films in particular stand out for one striking feature: the QSE is very robust for the Pb films, whose preferred thickness can be over 20 monolayers[21] (ML) Because of this, Pb films have been a focus of very intensive experimental and theoretical studies in recent years. This article also investigates Pb films and examines the role of the substrate in the film QSE by systematically studying Pb films on three different substrates with first-principles calculations.

A. Historical overview of Pb films

Historically, the QSE in the Pb films was first discovered in 1989, when Hinch *et al.* studied the low-temperature epitaxial growth of Pb on Cu(111).[28] In the last few years, with scanning tunneling microscopy (STM), photoemission spectroscopy, and other advanced experimental techniques, the Pb films have been studied in great detail, revealing some very interesting features. Budde *et al.* have observed that Pb islands of seven monolayers are preferred to form on the Si(111)-(7×7) substrate at low temperatures with low-energy electron diffraction[8] (LEED). Su *et al.* confirmed this with STM.[11] Hong *et al.*[14] studied the same system using real-time *in situ* x-ray diffraction, and their results show that the growth switches to a layer-by-layer mode for films of over five monolayers. Very recently, Özer *et al.*[21] made a comprehensive STM study of Pb films on three different semiconducting substrates, Si(111)-(7×7), Si(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$-α, and Ge(111)-($\sqrt{3}\times\sqrt{3}$)-α. It is found that Pb films have the same reentrant bilayer-by-bilayer growth mode on these three different substrates. Otero *et al.*[19] have investigated the Pb film growth on the metallic Cu(111) substrate with a range of Pb coverage from 4ML up to 22ML. Their study also indicates selective heights.

With the availability of atomically flat Pb films, an emerging trend in this particular field is to study other properties of these Pb films and see how the QSE plays a role in other aspects of Pb films besides growth. Guo *et al.*[2] have measured the critical temperature T_c of superconductivity for these Pb films and found that it oscillates with the film thick-

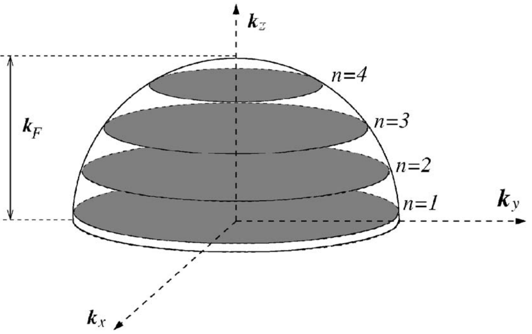

FIG. 1. Energy subbands of a metallic thin film.

ness. The superconductivity of these atomically flat thin metallic films has also been studied experimentally in Ref. 3. It is also found that electron-phonon coupling,[4] chemical desorption energy, and other properties have an oscillatory dependence on the film thickness. In addition, there have been experimental studies looking into the role of the QSE in the surface lattice relaxation.[29–32] There are ongoing efforts measuring the work functions of these atomically flat Pb films.[33]

The theoretical efforts can largely be grouped into two categories: one is analysis with the free-electron model;[22,24] the other is first-principles calculations.[34–38] The free-electron model is simple but captures the basic physics regarding the QSE: the formation of quantum-well states and the dependence of the surface energy on the film thickness. For example, within this model, one can easily understand the reentrant bilayer-by-bilayer growth mode of Pb(111) films on the semiconducting substrate:[21] For Pb(111), the ratio between the interlayer spacing d_0 (2.86 Å) and the Fermi wavelength E_F (3.66 Å) (Ref. 39) is approximately 3:4. This means that every two monolayers can accommodate comfortably three additional nodes of the standing wave formed by the electron at the Fermi level. As a result, Pb(111) films prefer energetically to grow bilayer by bilayer. Moreover, the ratio 3:4 is only approximate and there is a slight mismatch. This mismatch means a phase shift between two periodicities. As the film grows thicker, the phase shift can accumulate and cause the interruption of the bilayer-by-bilayer growth mode as observed in Ref. 21. Nevertheless, this model is too simple to present a clear picture how the QSE plays a role in other properties of the film, such as the superconducting T_c, surface lattice relaxation, and work function. Most importantly, this simple model is almost powerless to explain why the QSE in the Pb(111) film is so robust and exists in films as thick as 20–30 monolayers.[2,21] Friedel oscillations are discussed in Refs. 21 and 22 as a possible modification to this model.

At the other end is the study of the Pb film with first-principles methods. The advantage is that these *ab initio* methods can take into account all the necessary details of the system that have been ignored in the free-electron model. Furthermore, these methods allow one to study surface lattice relaxation, the work function, and other properties of the films, thus offering insights into the role of the QSE in these properties. So far, these studies have confirmed the bilayer-by-bilayer growth mode[34,36,37] and have either confirmed or predicted the oscillatory dependence of the surface relaxation and work function as a function of the film thickness.[34,36,37] However, the efforts are far from complete. One common shortcoming of all these studies is that the substrate is not properly included in the calculation. To accommodate the lattice mismatch between the Pb film and the substrate, some artificial and unphysical twists were introduced in these studies. In Ref. 36, the Si substrate was squeezed by 9% to fit the Pb film lattice, which makes Si metallic; in Ref. 34, the Pb film was compressed laterally to take into account the effect of Cu(111) substrate; in Ref. 37, the Cu(111) substrate was modeled with an effective potential.

B. Outline of the present investigation

In this article, we present a systematic and comparative *ab initio* study of three different Pb(111) films: free standing, on a Ge(111) substrate, and on a Cu(111) substrate. Because a vacuum is an insulator, our study can be also regarded as a comparative investigation of the properties of Pb(111) films on three different conducting substrates: insulator, semiconductor, and metal. Therefore, our results will offer a quite clear picture of the role of the substrate—that is, how the substrates affect the film properties differently due to their distinct conducting nature.

Our calculations are done for the surface energy, work function, and lattice relaxation. The surface energy is used to determine the stability of the Pb films. Our results show that these films share some common features, such as even-odd oscillations and the appearance of crossovers. However, our results also show some important differences among these films, such as the separation between the crossovers and the positions of the crossovers. In particular, we find that there are no even-odd oscillations in the surface lattice relaxation for the Pb/Cu(111) films. These differences are hard to understand in terms of the free-electron model, presenting a challenge to the existing understanding of Pb films. We point out that there is good reason to believe that our results for Pb films on the Ge(111) substrate may also be applied to the Si(111) substrate. The reason is that, as reported in Ref. 21, there is little difference between Pb films grown on Si(111) and Ge(111) substrates. This indicates that the Pb film properties are insensitive to some of the substrate details.

We emphasize that in our calculations there is no significant compression of either Pb film or substrates. The intrinsic conducting nature of the substrate is preserved. This is a substantial improvement over many previous studies,[34,36] where artificial compression is applied either to the film or to the substrate, as mentioned in the last subsection. For the Pb/Ge(111) film, we rotate the Ge substrate by 30°, which allows an almost perfect lattice match between the film and substrate. For the Pb/Cu(111) film, the lattice mismatch is solved by using a 3×3 Pb supercell and a Cu(111)-(4×4) substrate.

The remainder of the paper is organized as follows. In Sec. II, we describe in detail our *ab initio* calculations, especially how we overcome the lattice mismatch without significantly compressing either the film or the substrate for Pb/Ge(111) and Pb/Cu(111). In Sec. III, we present the surface energies for three different Pb films and compare them to the experimental results. At the beginning of this section, we discuss why the surface energy can be used to determine the film stability. In Sec. IV, we study the surface lattice relaxation. We have computed both the first interlayer spacing d_{12} at the surface and the second interlayer spacing d_{23} as functions of film thickness. In Sec. V, the work functions of these films are computed. Finally, we discuss and summarize our results in Sec. VI.

II. FIRST-PRINCIPLES METHOD

A. General description

Our first-principles calculations are based on density functional theory.[40,41] The Vienna *ab initio* simulation package (VASP) is used to solve the Kohn-Sham equations with periodic boundary conditions and a plane wave basis set.[42–44] To treat the electron exchange and correlation, we use the Perdew-Wang version[45] of the generalized gradient approximation (GGA). In our calculations, the 6*s* and 6*p* electrons of the Pb atom are treated as valence electrons and the 5*d* electrons treated as core electrons. For the Cu atom, the 3*d* and 4*s* electrons are used as valence electrons, and for the Ge atom the valence electrons are chosen to be the 3*s* and 3*p* electrons. Default plane-wave cutoffs (114 eV) from the GGA ultrasoft pseudopotential are used in our calculations.[46] We use the Monkhorst-Pack scheme[47] for the Brillouin zone sampling. To accelerate electronic relaxation, we apply the Fermi-level smearing approach of Methfessel and Paxton[48] with proper parameters. With the above setting, the lattice constants for bulk Pb, Ge, and Cu are found to be 5.04 Å, 5.76 Å, and 3.64 Å, respectively. The theoretical values are larger than the experimental values by 1.8% for Pb, 1.7% for Ge, and 1% for Cu.

In all the calculations, the spin-orbit coupling correction is neglected. Wei and Chou have included the spin-orbit coupling correction in their work,[36] and their results for free-standing Pb films are matched very well by our results without the coupling (see Fig. 5). This shows that the spin-orbit coupling is not important in the issues that we discuss in this article.

The Pb films on substrates can be dealt with two different models. One model is to keep the supercell size unchanged; Pb films of different heights are obtained by changing the thickness of the vacuum layer. In this model, the vacuum layer should be checked for the thickest Pb film to ensure that the system converges to a correct total energy. The other model keeps the thickness of the vacuum layer constant. As one increases the film thickness the size of the supercell is increased accordingly. We have checked both models carefully, and both of them lead to reliable results. The results presented in this paper are obtained with the latter model.

B. Specifics for different substrates

For free-standing Pb films, we use the 2×2 unit cell, where each layer contains four Pb atoms. The vacuum region is kept at 22 Å, which is thick enough for the system to converge to a correct total energy. The Brillouin zone sampling is done with 6×6×1 *k*-point meshes, and the results are checked by using 9×9×1 *k*-point meshes. The in-plane lattice constant of the Pb(111) slab is restricted to its theoretical bulk value. Along the [111] direction, the atoms are allowed to relax into their minimum-energy positions by fixing the positions of the atoms in the bottom layer. Energy convergence is reached when all the forces on the relaxed atoms are less than 0.01 eV/Å.

For Pb films on the Ge(111) substrate, there is a 11% mismatch between the lattice constants (Ge, 5.76 Å; Pb, 5.04 Å). This large mismatch makes it impossible to carry out directly first-principles calculations for the Pb(111) and Ge(111) interfaces. To overcome this obstacle, we rotate the substrate by 30°. In other words, in our calculation, the Pb(111) films are placed on a bulk truncated Ge(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ surface, as shown in Fig. 2. Such use of the 30° rotation enables us to accommodate the lattice mismatch between Ge and Pb, resulting a perfect lattice match at the interface after expanding the Ge lattice by only 1%. This rotation is rather artificial; however, the Ge substrate remains semiconducting. One may also artificially compress the substrate to match the lattice constants, such as for Si(111) substrate in Ref. 36. In this approach, the substrate may become metallic and change its conducting nature, which is not desirable. In our calculations, the Pb/Ge(111) system is modeled by a series of the 2×2 Pb supercell and a 10-layer Ge(111)-($\sqrt{3}\times\sqrt{3}$)$R30°$ substrate. For the Ge(111) layers, the six layers of Ge atoms near the Pb/Ge(111) interface are allowed to relax and the remaining four layers at the bottom are fixed at the bulk position. Besides, the Ge atoms at the bottom layer of the slabs are saturated with hydrogen. The vacuum layer is fixed at 19 Å. The 6×6×1 *k*-point sampling in the surface Brillouin zone is used in the calculation. Energy convergence is reached when all the forces on the relaxed atoms are less than 0.01 eV/Å.

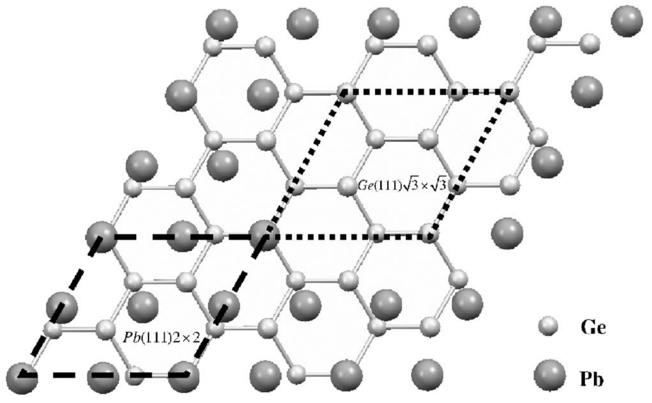

FIG. 2. Top view of the interface structure of Pb film on a Ge(111) substrate, showing the match between the $\sqrt{3}\times\sqrt{3}$ unit cell of Ge(111) and the 2×2 unit cell of Pb(111).

There is also a lattice mismatch for Pb films on the Cu(111) substrate. To accommodate this mismatch, we model the Pb/Cu(111) system by a 3×3 Pb supercell and a five-layer Cu(111)-(4×4) substrate, as shown in Fig. 3. This allows the Pb(3×3) unit cell to match very well with the Cu(4×4) unit cell only by expanding the in-plane Cu lattice constant by 3%. In fact, the STM, Auger electron spectroscopy (AES), and quantitative LEED studies[49–52] have revealed that the Cu(111) surface is nearly completely covered by a quasihexagonally close-packed Pb layer exhibiting a considerable vertical modulation and causing a pronounced (4×4) superstructure, in which 9 Pb atoms are accommodated in the (4×4) supercell containing 16 Cu atoms.

To identify the influence of expanding the Cu lattice constant, we have calculated the band structure of Cu after expanding the lattice constant by 3%, which is found to be very close to the ideal bulk. In our calculations, the Cu atoms in the above three layers are allowed to relax and those in the bottom two are fixed at the bulk position. The vacuum layer is restricted to about 19 Å. The 3×3×1 *k*-point sampling in the surface Brillouin zone is used, and the result is carefully checked by 5×5×1 *k*-point sampling. Energy convergence

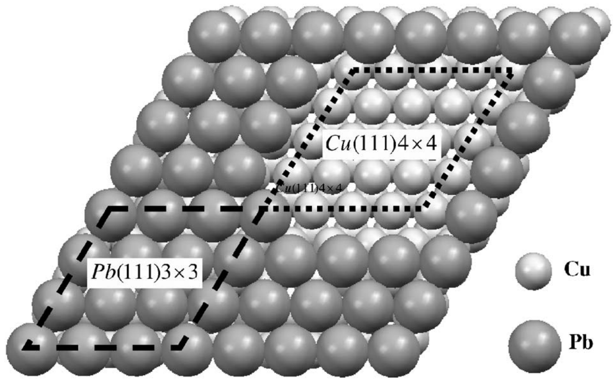

FIG. 3. Top view of interface structure of Pb on Cu(111). It shows the match between the 4×4 unit cell of Cu(111) and the 3 ×3 unit cell of Pb(111).

is reached when all the forces on the relaxed atoms are less than 0.01 eV/Å.

III. FILM STABILITY AND SURFACE ENERGY

As mentioned in the Introduction, there are now numerous experiments showing that Pb films (or Ag films) of certain monolayers can form after annealing. For example, in Ref. 21 only 5, 7, 9,… monolayers of Pb films on top of the wetting layers are observed on the Si(111)-(7×7) substrate by the STM. All these observations indicate that films of preferred thickness are favored energetically and they are stable or sufficiently metastable while other films are unfavored energetically and unstable against annealing. Therefore, to study the film stability, we need to analyze the film's energy and use it to judge whether the film is stable or unstable. It is then necessary that we pause here to discuss the criterion of film stability in terms of energy before we present our results from the first-principles calculations.[22]

A. Film stability criterion

As a given amount of a certain material is deposited on a substrate, many different types of films can form. In this article, we focus on the continuous films seen in Fig. 4. During annealing at certain temperatures, the film will likely change its morphology. The driving force behind the change is thermodynamics: a system always evolves to a morphology of lower energy when it is allowed by growth kinetics. The configuration that is a local minimum of the system energy is relatively stable and will likely be the outcome of annealing. So, to theoretically determine the film stability or predict how the film shapes up after annealing, we need to find the system energies of different configurations and compare them.

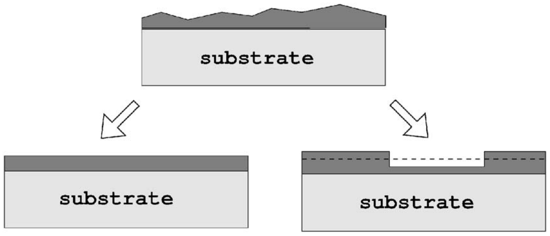

FIG. 4. Continuous thin film. The top is a rough film before annealing; after annealing, the film may become atomically flat (bottom left) or a film of two different heights (bottom right). In this case, the contact area between the film and substrate is conserved during the morphological evolution.

For the continuous film in Fig. 4, after annealing, the whole film may become atomically flat, having the same height everywhere, or the film may evolve to have two different heights (or other morphologies). This depends on which configuration has a lower system energy E_t. An atomically flat film is possible when $E_t(\text{left}) < E_t(\text{right})$, where $E_t(\text{left})$ is the energy for the film on the bottom left in Fig. 4 and $E_t(\text{right})$ is for the film on the bottom right. If S is the total contact area of the film with the substrate, then we have $E_t(\text{left}) = SE_s(N)$ and $E_t(\text{right}) = E_s(N+1)S/2 + E_s(N-1)S/2$ with E_s being the surface energy per unit area of a film. Therefore, the criterion for the stability of an atomically flat film of N monolayers is

$$E_s(N) < \frac{E_s(N+1) + E_s(N-1)}{2}. \qquad (1)$$

This criterion motivates us to define a new quantity, the second difference of E_s:

$$\Delta^2 E(N) = E_s(N+1) + E_s(N-1) - 2E_s(N). \qquad (2)$$

According to the criterion (1), a film of N monolayers is stable when $\Delta^2 E(N) > 0$ and unstable otherwise. As a film grows thicker, its properties become more and more like a bulk. In other words, for a thick film, its properties should change little with the addition or removal of one monolayer. Therefore, we expect that for large N the second difference $\Delta^2 E$ is very small, $|\Delta^2 E(N)| \ll 1$. Reversely, when we have $|\Delta^2 E(N)| \ll 1$ for a given layer number, we say that the film of N monolayers is bulk like. The films grown in Refs. 5, 7, and 21 are continuous films.

B. Surface energy of Pb films

In our *ab initio* calculations, the surface energy of a Pb film is computed as follows. We first calculate the total energies of films of different thickness. This total energy can be viewed as consisting of two parts: one is the energy of bulk Pb with the same thickness and the other is a small deviation from this energy caused by the two film interfaces. As a result, these total energies should increase linearly with the film thickness modulated by some small fluctuations. We then fit the data with a linear function. After subtracting the linear part from the total energies, we are left with the small fluctuations, which are the desired surface energies E_s.

We study first the free-standing Pb film. Even though it is impossible to grow free-standing films with current technology, the theoretical study of such films is still of great value. Most of all, it offers a reference point for films with substrates such that the effects of substrates can be analyzed and extracted by comparison.

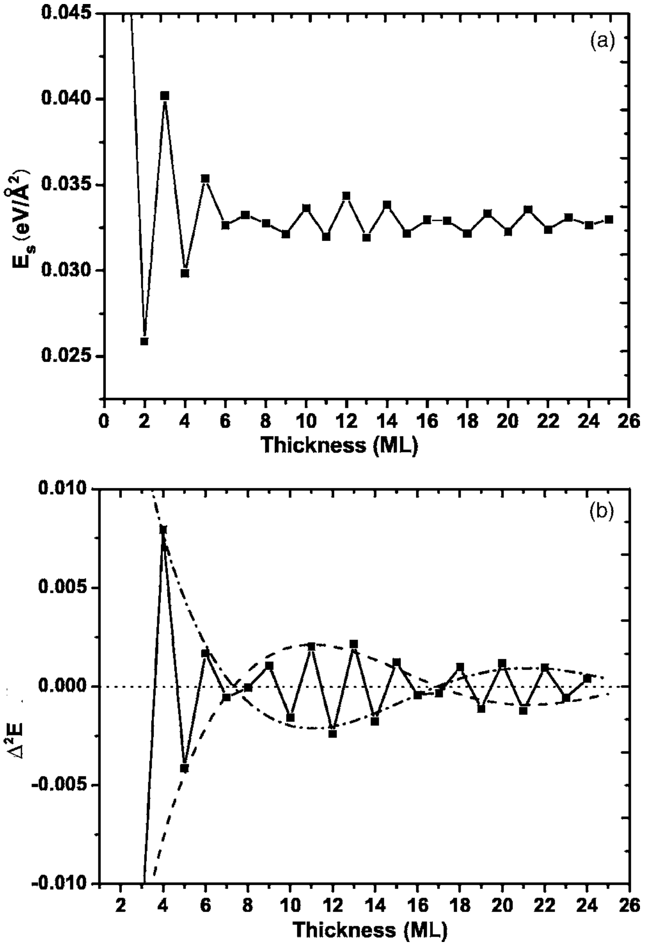

FIG. 5. (a) Surface energies of free-standing Pb films. (b) The discrete second derivative of surface energy of free-standing Pb films.

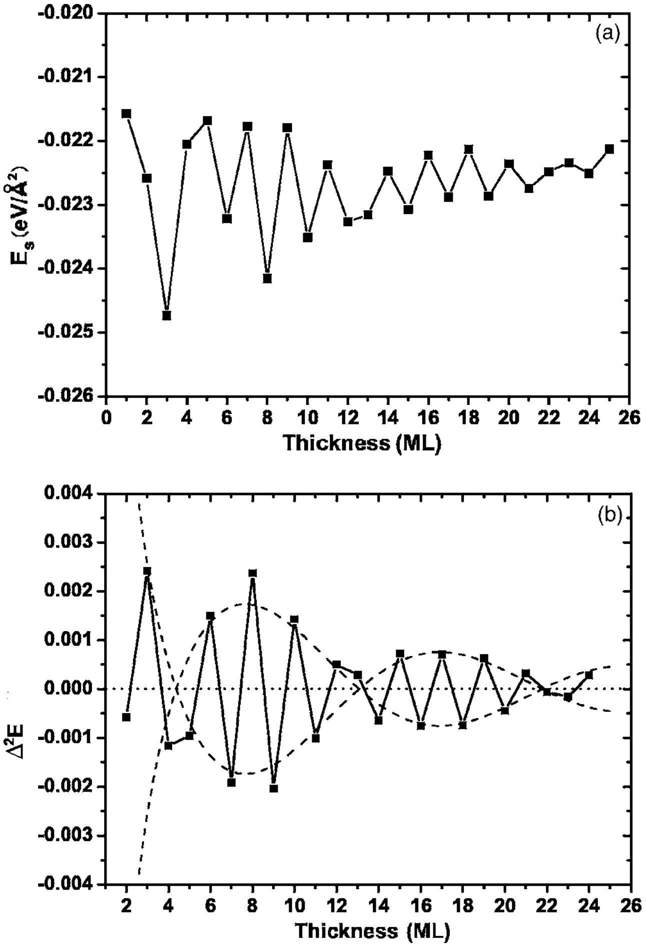

FIG. 6. (a) Surface energies of Pb(111) films on a Ge(111) substrate. (b) The second derivative of surface energy of Pb(111) films on a Ge(111) substrate.

Shown in Fig. 5 are the surface energies of free-standing Pb films and their discrete second derivatives, respectively. The surface energy oscillates mostly with film thickness in a bilayer fashion. However, this bilayer pattern is interrupted at least twice by crossovers at films of 8 layers and 17 layers, as seen in Fig. 5. The separation between the neighboring crossovers is 9 monolayers. It is rather striking that the oscillation with film thickness persists for films as thick as 26 monolayers. According to the stability criterion of Eq. (1), it is clear from Fig. 5(b) that the films of 4, 6, 9, 11, 13, 15, 18, 20, and 22 layers are stable. These results agree well with Ref. 36.

The surface energies of Pb films on Ge(111) substrate and their discrete second derivatives are plotted in Fig. 6. Similar to the free-standing films, there are bilayer oscillations interrupted by crossovers. The separation between the crossovers is about 9 monolayers but the crossovers are located at 5 monolayers, 13 monolayers, and 23 monolayers, which are

TABLE I. Stabilities of Pb(111) films on three different substrates. "s" stands for stable and "u" for unstable. The crossover points are indicated by boldfaced letters.

Substrate		Layer numbers of Pb films																					
		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Free standing		u	s	u	s	u	**u**	s	u	s	u	s	u	s	u	**u**	s	u	s	u	s	u	s
Ge(111)	Experiment[a]			**s**	s	u	s	u	s	u	s	u	**s**	s	u	s	u	s	u	s	u	**u**	s
	This work	s	u	**u**	s	u	s	u	s	u	s	**s**	u	s	u	s	u	s	u	s	u	**u**	s
Cu(111)	Experiment[b]			**u**	s	u	s	u	s	s	u	s	u	s	u	s	bulk-like						
	This work	s	u	**u**	s	u	s	u	s	u	**u**	s	u	s	u	s							

[a] References 8 and 21.

[b] Reference 19.

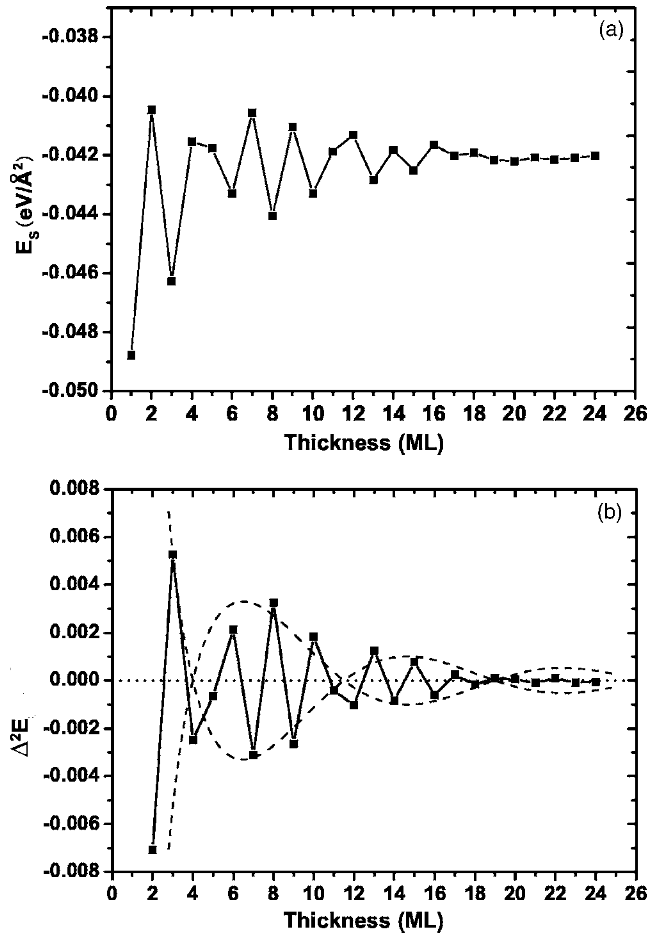

FIG. 7. (a) Surface energies of Pb(111) films on a Cu(111) substrate. (b) The second derivative of surface energy of Pb(111) films on a Cu(111) substrate.

different from the free-standing case. With Eq. (1), we find from Fig. 6(b) that the films are stable at 3, 6, 8, 10, 12, 15, 17, 19, and 21 layers. This agrees almost perfectly with a recent experiment of Pb films on the Ge(111) substrate.[21] This indicates that our first-principles calculations have captured essential physics.

For a metallic substrate, we have studied Pb films on Cu(111) substrate, which has been carried out in experimental studies. Our first-principles results for Pb on Cu(111) substrate are shown in Fig. 7; there are similar even-odd oscillations punctured by crossovers. We find that the stable films on the Cu(111) substrate are of 3, 6, 8, 10, 11, 13, 15, and 17 layers, which agree very well with the experimental results[19] (see Table I).

For easy comparison, we have built a stability table for the three different Pb films in Table I. It is clear from the table that the free-standing Pb film and the film on Ge(111) substrate have very similar oscillation patterns in terms of stability. They differ from each other only by a "phase shift" of two layers. It seems to indicate that the substrate only affects the film stability by a phase shift. However, the Pb films on Cu(111) substrate are quite different from these two films: (i) The crossovers occur at 5 monolayers and 12 monolayers, which separate from each other by only 7 monolayers instead of 9. (ii) The oscillations level out already at 18 monolayers.

C. Discussion

Can we at least understand the above *ab initio* results qualitatively with the aforementioned free-electron model? The Pb films on Cu(111) presents a challenge. According to the free-electron model, the bilayer oscillations are the results of the ratio $k_F : k_{BZ} \approx 4:3$ ($k_{BZ} = \pi / d_0$) in Pb(111) films. However, this ratio is only approximate and the small deviation from the exact 4:3 ratio will accumulate as the film grows thicker, leading to the appearance of crossovers. The beating period of the crossovers is then given by

$$\lambda_{\text{beat}} = \frac{\pi}{3k_{BZ} - 2k_F}. \qquad (3)$$

Since k_{BZ} does not change, the difference in the beating periods of Pb films can only be caused by the change of k_F due to different substrates. The Pb films on Cu(111) have a beating period of 7 instead of 9 for the other two kinds of films. Simple calculations indicate that k_F should be decreased by about 1.3% by the Cu(111) substrate. This in turn means that there should be an electron density change of ~4% in the Pb films, which is certainly very unlikely. A more sophisticated theory is needed here.

We note that the envelopes of oscillation patterns of the discrete second derivative of surface energy in Figs. 5–7 have been fitted with a Friedel-oscillation-like form,[36]

$$E_s = A\frac{\cos[2k_F(N + \Delta N)d_0]}{(N + \Delta N)^{\alpha}} + B, \qquad (4)$$

where α, A, and B are constants. The envelope functions of the discrete second derivative of surface energy are shown in Figs. 5(b), 6(b), and 7(b). The fitting shows that the period of beating is 9.1 monolayers, 8.7 monolayers, and 7.2 monolayers for the free-standing film, Ge(111) substrate, and Cu(111) substrate, respectively. This is consistent with our direction

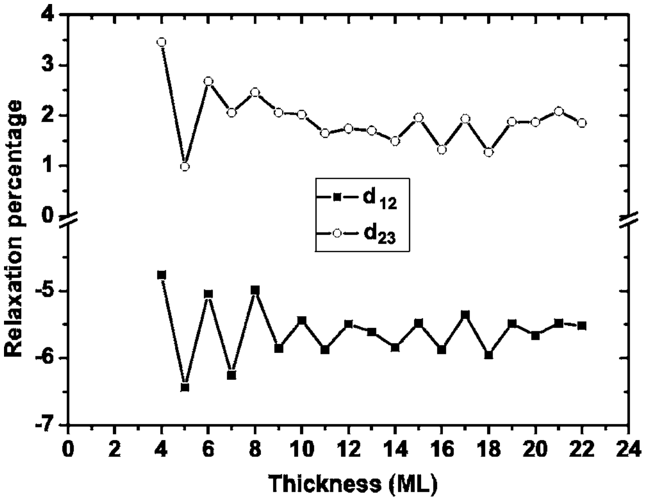

FIG. 8. Relative interlayer spacings d_{12} and d_{23} of free-standing Pb films.

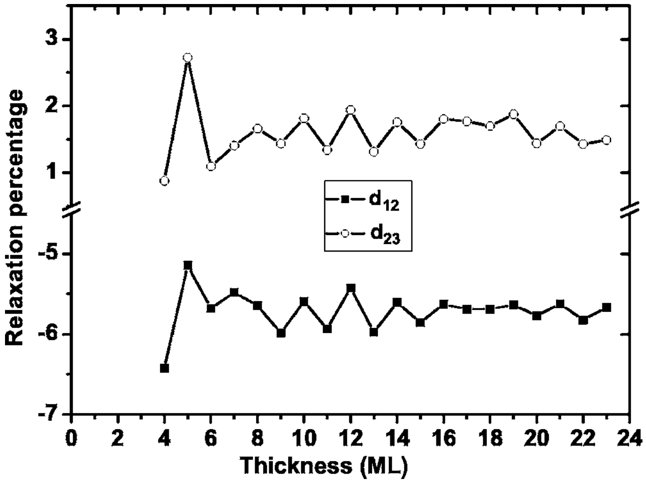

FIG. 9. Relative interlayer spacings d_{12} and d_{23} of Pb films on a Ge(111) substrate.

observation that the beating periods of the free-standing films and films on Ge(111) substrate are 9 monolayers while the films on Cu(111) substrate have a period of 7 monolayers.

IV. LATTICE RELAXATION

Due to a very different geometric environment, the lattice spacings near a surface can be very different from the corresponding bulk value. This phenomenon is called surface lattice relaxation.[53–55] There have been some efforts recently, mostly on Pb films, to study the quantum size effect on the surface lattice relaxation—that is, how the lattice spacings of the first few layers near the surface depend on the film thickness. With various experimental techniques, such as helium atom scattering, STM, and x-ray diffraction, one has observed that the surface lattice relaxations of Pb films on different substrates, Si(111), Cu(111), and Ge(001), are functions of the film thickness, oscillating strongly with the film thickness.[20,30,31] A very recent experiment with LEED shows clearly that the first layer spacing d_{12} of the Pb film on the Si(111)-(7×7) oscillates in a perfect even-odd fashion from 4 to 10 monolayers.[32] On the theoretical side, the most extensive study was done for the Pb/Cu(111) films,[34] where a similar oscillation of d_{12} with layer number was also found.

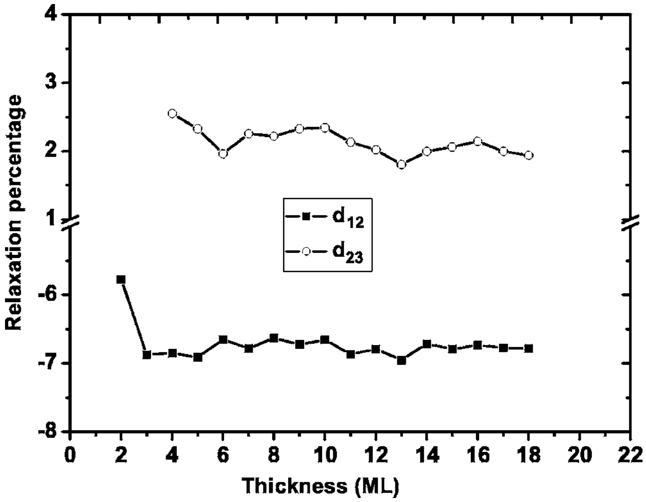

FIG. 10. Relative interlayer spacings d_{12} and d_{23} of Pb films on a Cu(111) substrate.

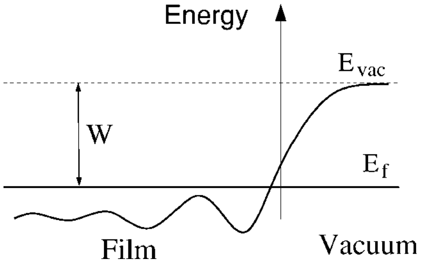

FIG. 11. Schematic drawing of energies at a film surface. The solid curve represents the electrostatic potential across the film surface. The oscillations in the potential are caused by the Friedel oscillations of the surface electron density. Its value deep in the vacuum side is usually called the vacuum energy.

In our calculation, the interlayer relaxation in a film of n monolayers is defined as

$$d_{m,m+1} = \frac{Z_m(N) - Z_{m+1}(N) - d_0}{d_0} \times 100, \qquad (5)$$

which is a percentage measurement for the lattice relaxation between the mth and $(m+1)$th layer. $Z_m(N)$ is the position of the ion in the mth layer along the z direction.

Plotted in Fig. 8 are our *ab initio* results of the first two interlayer spacings d_{12} and d_{23} of free-standing Pb films. From the figure, we see that the first interlayer spacing d_{12} contracts by about 5.5% relative to the bulk value of the lattice constant while the second interlayer spacing d_{23} expands by about 1.5%. These results are in good agreement with a recent LEED experiment,[32] which finds that $d_{12} = -3.5\%$ and $d_{23} = 1.9\%$. It is a common feature of Pb films of all thickness that the first interlayer spacing contracts and

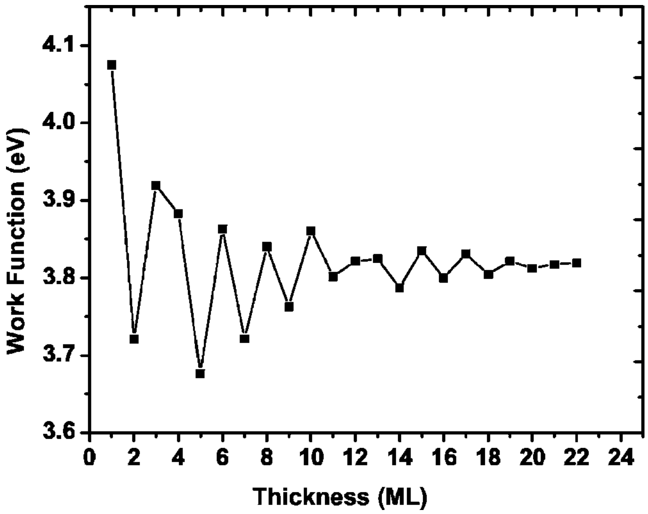

FIG. 12. Work functions of free-standing Pb films.

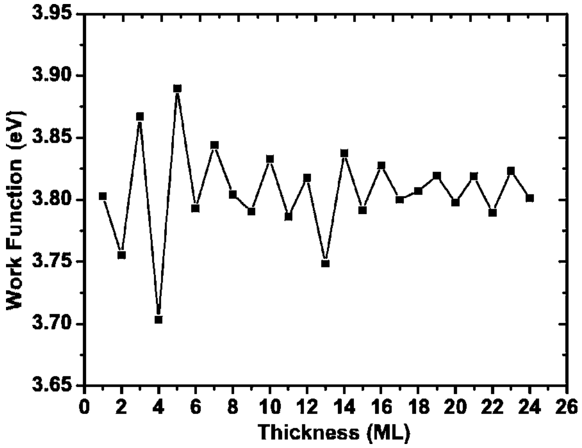

FIG. 13. Work functions of Pb films on a Ge(111) substrate.

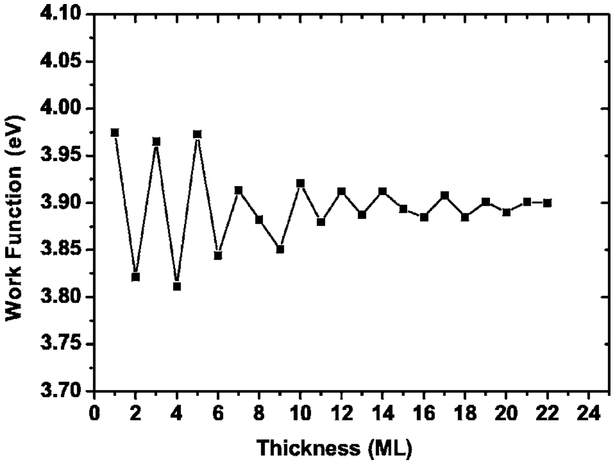

FIG. 14. Work functions of Pb films on a Cu(111) substrate.

the second interlayer expands. Nevertheless, as we see in Fig. 8, the exact percentage of contraction or expansion oscillates with the film thickness. The oscillation is again a bilayer one with crossovers. However, there is only one obvious crossover at the film of 13 monolayers.

For Pb films on Ge(111) substrate, our results of the lattice relaxation d_{12} and d_{23} are plotted in Fig. 9. They are very similar to the free-standing case, exhibiting bilayer oscillations with crossovers. In particular, the oscillations in d_{23} are more pronounced. Also due to a "phase shift," the positions of the crossovers are different. There are two apparent crossovers at 7 and 17 layers.

The lattice relaxation of Pb films on Cu(111) is quite different from the above two cases. As seen in Fig. 10, there are no obvious bilayer oscillations in both d_{12} and d_{23}. Moreover, the oscillations have rather small amplitude and are without any discernible pattern. It is quite challenging to understand this behavior with the free-electron model.

V. WORK FUNCTION

The work function is a basic property of a film surface. In the last section, we have seen that the film stability depends strongly on the film size as the film surface energy oscillates with the film thickness. It is natural to expect that the work function also relies on the film thickness, deviating from its standard value which is defined for a semi-infinite film.[56] In our numerical calculations, the work function W is computed as the difference between the vacuum energy E_{vac} and the Fermi energy E_f as shown in Fig. 11.

Plotted in Fig. 12 are the work functions of free-standing Pb films. We indeed see bilayer oscillations, which are interrupted twice by crossovers. The crossovers are at layer 4 and layer 13, different from the surface energy. However, the two crossovers are separated by 9 monolayers, the same as for the surface energy. Also, we notice that the oscillations decay slightly faster: there are no clear oscillations beyond 20 monolayers.

The work functions for the Pb films on Ge(111) substrate are shown in Fig. 13. The results oscillate bilayerly with crossovers. The crossovers are at 9 monolayers and 18 monolayers, which are different from the free-standing films.

We have also computed the work function of Pb films on the metallic Cu(111) substrate. The results are illustrated in Fig. 14. The QSE is evident with the work function oscillating with large amplitudes in the familiar even-odd fashion. The bilayer oscillating pattern is interrupted by two crossovers at 8 and 15 layers. That is, the separation between the two crossovers is 7 layers, identical to that of the surface energy.

VI. DISCUSSION AND SUMMARY

In summary, we have studied with first-principles methods the quantum size effect of three different types of Pb films: free standing, Pb on Ge(111), and Pb on Cu(111).

TABLE II. Crossover positions of Pb(111) films on three different substrates for three different properties. The experimental values are from the same sources as in Table I.

		Free standing			Ge(111)			Cu(111)		
		First	Second	Third	First	Second	Third	First	Second	Third
E_s	This work	8	17		5	13	23	5	12	
	Experiments				5	13		5	12	
W	This work	4	13		9	18		9	16	
d_{12}	This work		13		8	17				

Three important properties of the films are computed: they are surface energy, surface lattice relaxation, and work function. As we have shown, there is a significant QSE in all these properties for all the Pb films studied. Furthermore, except for the lattice relaxation in Pb films on Cu(111), there is a common feature among the QSE: it oscillates in a bilayer fashion with a few widely separated crossovers. However, due to the distinct conducting nature of the films, the oscillation pattern differs among Pb films in some important features, such as the locations of crossovers and the separation between crossovers. For clarity, these differences are listed in Table II.

From this table, we notice that there is a clear correspondence between lattice relaxation and work function as their crossover positions are very close to each other. This is understandable since the lattice relaxation and work function are all closely related to the charge redistribution near the surface. This relation was noted in Ref. 32. We also notice that the crossover positions for the lattice relaxation and work function lie almost perfectly between the crossover positions for the surface energy. This may indicate that if the dependence of the surface energy on the film thickness x is given by $E_s(x)$, then both the lattice relaxation and work function should depend on the film thickness in the form of $dE_s(x)/dx$.

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