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PAPER

Thickness dependent of phase shift between surface energy and work function in Pb ultrathin films

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Abstract

Through first-principles calculations within density functional theory, the phase shift between surface energy and work function in FCC (111) and HCP (0001) Pb and $\text{Pb}_{1-x}\text{Bi}_x$ alloy films has been investigated. Deviating from the previously described $\pi/2$ phase mismatch between the surface energy and work functions, an additional phase shift of about one monolayer is identified at small thickness of the Pb and Pb alloy films. The additional phase shift depends on the film thickness and will disappear as thickness increases. Moreover, we give an interpretation of the one-monolayer deviation in the framework of the free electron model, attributing it to the unique structure of the Fermi surface in Pb ultrathin films.

1. Introduction

Quantum size effects (QSEs), which enable us to control the material size at the nanoscale level to achieve desired functionalities within quantum engineering, are one of the hottest issues in both nanoscience and nanotechnology. In the study of QSEs of ultrathin films, the phase relationship between the quantum oscillation of surface energy and work function has gained tremendous interest and has been consistently reported from both theoretical and experimental standpoints [1–4]. In experiments, photoemission studies of the Ag/Fe (100) system have provided supporting evidence about this phenomenon; surface energy [5] and work function [6] were measured separately and the phase relationships between them were presented. When preparing Ag films on Fe (100), films of 2 ML (monolayer) and 5 ML thickness are structurally stable, whereas films with other thicknesses are unstable and will bifurcate into films with an $N \pm 1$ monolayer. However, at 2 ML and 5 ML, Ag films have a lower work function than at other thicknesses. Thus, it was concluded that in the ultrathin films, surface energy oscillation and the oscillation of work function are not in phase as they are in bulk materials. Then density functional theory (DFT) calculations were performed in both film-substrate and film-vacuum interfaces, and the results supported the phase shift phenomenon [7].

Another typical material that exhibits strong QSE is the Pb(111) ultrathin film, where the accidental matching of Fermi wavelength and the lattice space, $3\lambda_F/2 \approx 2$ ML, results in bilayer oscillation of both surface energy and work function [1, 2]. Meanwhile, the slight deviation from the exact matching will result in a beating pattern with a period of about 9 ML, which is given by $\lambda_{\text{beating}} = \pi / |3k_{\text{BZ}} - 2k_F| \approx 9.3$ ML, where $k_{\text{BZ}} = \pi/d_0$ and d_0 is the lattice space. As in the Ag films, a phase mismatch between surface energy and work function was found again in Pb ultrathin films in many experiments [8–11] and theoretical studies [1–3, 12]. By using an STM tip to examine the local work function of Pb islands on vicinal Si(111) 7×7 substrate and using scanning tunneling spectroscopy (STS) to track the evolution of the quantum well states, Xue *et al* first found that the highest occupied quantum well states have the same oscillatory behavior as the local work function and are perfectly anti-correlated. Thus, a larger local work function corresponds to a lower highest occupied quantum well state [13], which directly indicates that the oscillations of work function and surface energy are not in phase

and that the phase shift should have a certain relationship. In theory, the free electron model has been employed by T C Chiang *et al* to try and account for this phase shift. Their calculations show that surface energy and work function oscillate with sinusoidal and cosine functions respectively, where oscillations in the surface lead to oscillations in work function by $\pi/2$ (1/4 of a period) [4]. However, there are still some unresolved puzzles in the phase relation between them; in particular we noticed that there is always a clear deviation from the $\pi/2$ phase rule both in first-principles studies and in experiments.

As can be seen in our previous work, doping could tune the QSEs in the FCC PbBi (111) ultrathin films, such as film stability and oscillation pattern, by changing the Fermi vector [12, 14]. In this paper, we continue our work on the calculations of the QSEs in FCC PbBi (111) alloy films with higher doping contents and in HCP PbBi (0001) films. From a comprehensive examination of the phase relationship in the two different structures with different Bi contents, we find that the $\pi/2$ phase shift rule deviates for all pure and alloy ultrathin PbBi films. A novel new phase shift of $\pi/2 - \delta$ is obtained, where the additional phase shift δ decreases with layer number and will vanish at large layer numbers. To discover the underlying physical reason, we performed a free electron model calculation and, surprisingly, found that the theoretical results agree perfectly with our DFT simulation and explain the appearance of the thickness-dependent additional phase shift δ .

2. Methods and calculations

In the implementation of our first-principles calculations, we used a Vienna *ab-initio* simulation package (VASP) to solve the Kohn–Sham equations within the framework of density function theory [15, 16]. In the description of the electron exchange and correlation, the Perdew–Wang version [17] of the generalized gradient approximation (GGA) is adopted. The Monkhorst–Pack [18] scheme is employed in the Brillouin zone sampling and the Fermi-level smearing approach of Methfessel and Paxton with proper parameters [19] is applied to accelerate electronic relaxation. For the Pb and Bi atoms, the 6s and 6p electrons are treated as valence electrons and the 5d electrons are treated as core ones. Spin-orbital coupling is neglected because it is unimportant in this issue [12].

To study the QSEs of PbBi alloy films, we use different kinds of supercells with proper distribution of dopants to simulate different compositions. The vacuum layer between neighboring periodic slabs is fixed at 10 ML. The Brillouin zone sampling is carried out with $9 \times 9 \times 1$ k-point mesh and the results are checked by $21 \times 21 \times 1$ larger meshes. In our calculation, all the atom positions are relaxed until energy convergence, where all the forces on the atoms are less than 0.01 eV Å.

The surface energy is obtained by subtracting the bulk energy from the total energy. This is because the total energy consists of two parts: the linear increasing bulk energy and the small deviation caused by the film interfaces [20, 21]. In this paper, to study the stability of the films, we thereby use a more helpful quantity: the second-order derivative of the surface energy $\Delta^2 E_S(N)$ [8], which is expressed as

$$\Delta^2 E(N) = E_S(N+1) + E_S(N-1) - 2E_S(N). \quad (1)$$

A positive $\Delta^2 E_S(N)$ indicates a local minimum of system energy and thus the film is relatively stable compared to its neighbors; otherwise it is unstable [8, 23]. We note that the second-order derivative basically has an inverse oscillation pattern compared with surface energy; this is a more direct way to judge the stability of the films. As the film grows thicker, the properties of the film approach to its bulk and change little with 1 ML variation. In this situation, the film will grow layer by layer and the second-order derivative is expected to be very small.

The work function is obtained by subtracting the Fermi energy from the vacuum level energy, where vacuum level energy is obtained from the electrostatic potential perpendicular to the film and the Fermi energy is read from the static computation results.

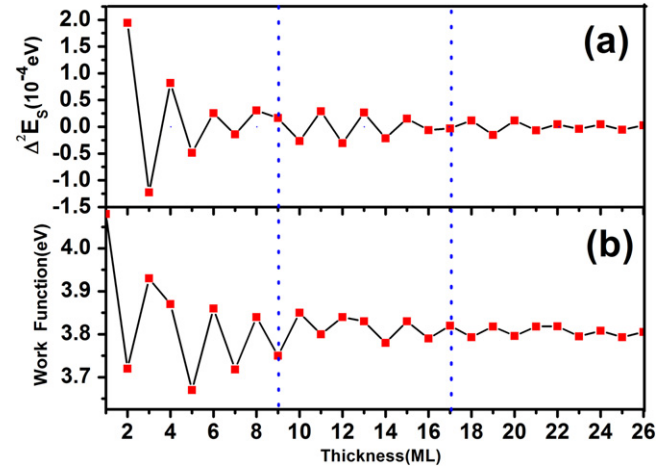
3. Results and discussion

3.1. Phase relation between surface energy and work function in FCC $\text{Pb}_{1-x}\text{Bi}_x$ (111) alloy films

We start by calculating the lattice constants of FCC films with different doping concentrations. The 4×4 supercell with one atom replaced by Bi is chosen to describe $\text{Pb}_{0.94}\text{Bi}_{0.06}$ alloy films. The 3×3 unit cell is chosen and we replaced 1, 2 and 3 atoms respectively to simulate the 11%, 22% and 33% Bi contents. 14% and 25% Bi contents are obtained by replacing one atom in the $\sqrt{7} \times \sqrt{7}$ and 2×2 unit cells, respectively. Since the doping positions have been confirmed to have a marginal impact on the result [13], in our study we chose the distributions that maximize the Bi spacing in order to minimize the interaction of Bi atoms. The distance between Bi atoms in two neighboring layers is larger than 0.6 nm; therefore, the interaction between the Bi atoms is assumed to be sufficiently weak. By using an interpolation method and minimizing the total energy of

Table 1. Lattice constants of FCC(0001) $\text{Pb}_{1-x}\text{Bi}_x$ alloy with different Bi content.

Density	0%	6%	11%	22%	25%	33%
$a/\text{\AA}$	5.04	5.048	5.056	5.060	5.063	5.066

**Figure 1.** Second-order derivative of surface energy (a) and work function (b) of pure FCC Pb(111) films. The dotted lines are lined up with adjacent crossovers in $\Delta^2 E_s(N)$ to highlight the phase shift between $\Delta^2 E_s(N)$ and work function.

the supercells, the lattice constants of the alloys with different doping levels are calculated as shown in table 1. With more Bi doped into the alloy, as seen from table 1, the lattice constants will be only slightly larger than those of pure Pb.

The first-principles calculations of the second-order derivative of surface energy and work function of pure FCC Pb(111) films are shown in figure 1. As is well known, the accidental matching of the Fermi wavelength and the interlayer space along (111) result in the approximately bilayer oscillation of both of the two quantities. And because the Fermi wavelength and the interlayer space are not exactly commensurate, the slight departure will lead to a beating pattern with a superperiod of 9.3 ML. The first crossovers of $\Delta^2 E_s(N)$ are located at 9 ML, while for the positions of the crossover of work functions, they are at 4 ML and 13 ML respectively. The phase shift between $\Delta^2 E_s(N)$ and work function is about 4 ML. The phase of the beating pattern of work function is $(9.3/2 - 1)$ ML ahead of that of $\Delta^2 E_s(N)$, namely, $\pi/2 - \delta$, where δ corresponds to the phase shift of 1 ML.

Since the phase shift is caused by the mismatch between the Fermi wavelength and lattice spacing in Pb(111) films, it is natural to conclude that the phase shift will change with the mismatch between the Fermi wavelength and lattice spacing. To demonstrate this, we changed the mismatch between the Fermi wavelength and lattice spacing by doping the Bi atom in Pb(111) films. Figure 2 presents the surface energy and work function of $\text{Pb}_{0.89}\text{Bi}_{0.11}$ up to 28 monolayers. As with pure Pb(111) ultrathin films, the bilayer oscillations of PbBi(111) alloy films are well preserved up to 28 ML. As seen in figure 2, the beating period of the QSEs become larger, namely 14 ML, with crossovers of the 12, 26 layer for $\Delta^2 E_s(N)$ and the 6, 20 layer for work function, respectively. The phase shift of the crossovers between them is 6 ML, which is exactly $(14/2 - 1)$ ML. As in the pure Pb(111) situation, there is again one additional layer of phase discrepancy from $\pi/2$. In further study, this departure from the $\pi/2$ phase rule is also observed in $\text{Pb}_{1-x}\text{Bi}_x$ (111) alloy films with other Bi contents. In table 2 we list the crossovers of different $\text{Pb}_{1-x}\text{Bi}_x$ (111) alloy films to make a better comparison. The beating period will change with Bi content. However, the phase mismatching between them is always $\pi/2 - \delta$.

3.2. Phase relation between surface energy and work function in HCP PbBi (0001) alloy films

In this section, to further verify the phase relation between surface energy and work function in different structures, we also study the QSEs in the HCP $\text{Pb}_{1-x}\text{Bi}_x$ (0001) alloy films. Since previous work has focused only on FCC films, here we first investigate the QSEs of a pure HCP Pb (0001) structure. In figure 3, we present $\Delta^2 E_s(N)$ and the work function of HCP Pb(0001) films with different layer numbers. Bilayer periodicity in both $\Delta^2 E_s(N)$ and work function with interruption of crossovers clearly manifests the QSEs of HCP Pb(0001) films. Like its FCC (111) partner, the bilayer oscillation is induced by the almost perfect harmony between lattice spacing and Fermi wavelength, while the slight mismatch leads to the beating pattern.

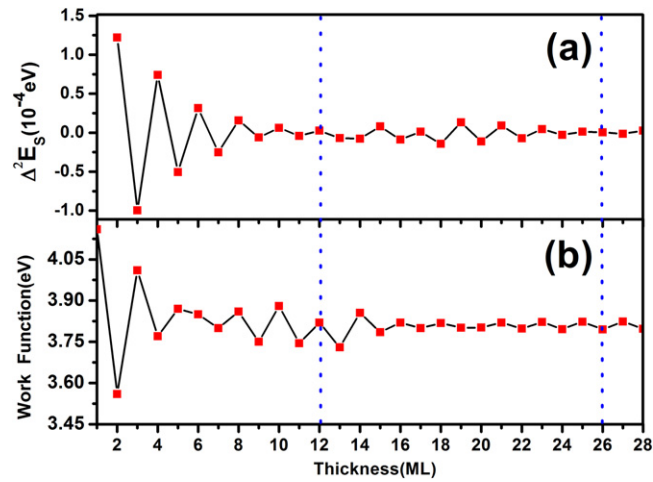


Figure 2. Second-order derivative of surface energy (a) and work function (b) of FCC $\text{Pb}_{0.89}\text{Bi}_{0.11}$ (111) films. The dotted lines are lined up with adjacent crossovers in $\Delta^2 E_s(N)$ to highlight the phase shift between $\Delta^2 E_s(N)$ and work function.

Table 2. Crossovers of $\Delta^2 E_s(N)$ and work function in FCC PbBi alloy films. S_1 and S_2 are ‘First Crossover’ and ‘Second Crossover’ of the second-order derivative of surface energy, respectively, and W_1 and W_2 represent ‘First Crossover’ and ‘Second Crossover’ of work function. Phase Mismatching and Crossover are given in the last two lines of the table.

x	0%	6%	11%	14%	25%	33%
S_1	9	10	12	14	26	20
S_2	18	20	26			
W_1	4	6	6	8	14	11
W_2	13	16	20	22		
Crossover	9	10	14	14	26	20
Phase Mismatching	$4 \approx 9/2-1$	$4 = 10/2-1$	$6 = 14/2-1$	$6 = 14/2-1$	$12 = 26/2-1$	$9 = 20/2-1$

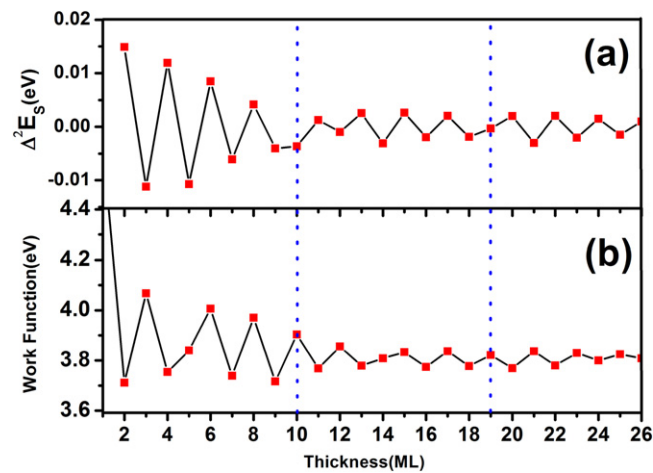


Figure 3. Second-order derivative of surface energy (a) and work function (b) of pure HCP Pb (0001) films. The dotted lines are lined up with adjacent crossovers in $\Delta^2 E_s(N)$ to highlight the phase shift between $\Delta^2 E_s(N)$ and work function.

In the study of the alloy films with Bi doping, the bilayer oscillations were also well preserved up to 44% Bi content. As in the FCC situation, 6%, 11%, 25% and 33% doping concentrations were obtained by one atom doping in different supercells. Moreover, we chose 3×3 supercells and replaced 2 and 4 atoms to simulate 22% and 44% doping contents, respectively. Lattice constants of different alloy films are shown in table 3. Both a and c will change with Bi doping, while the variation is very small.

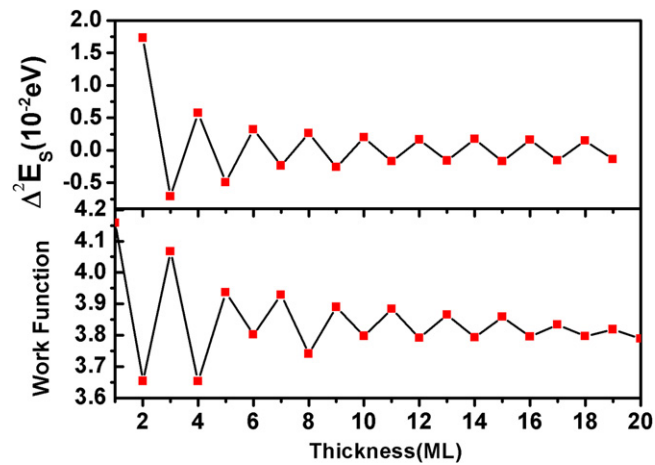
Since doping Bi atoms can increase the electron density and thus the Fermi wave vector, the mismatching between Fermi wave vector and lattice space is then reduced. Consequently, the beating period

Table 3. Lattice constants of HCP(0001) $\text{Pb}_{1-x}\text{Bi}_x$ alloy with different Bi content.

Density	0%	6%	11%	22%	25%	33%	44%
$a/\text{\AA}$	3.536	3.552	3.543	3.539	3.534	3.586	3.657
$c/\text{\AA}$	5.905	5.852	5.864	5.885	5.916	5.752	5.828

Table 4. Crossovers of $\Delta^2 E_s(N)$ and work function in HCP PbBi alloy films. S_1 and S_2 are ‘First Crossover’ and ‘Second Crossover’ of the second-order derivative of surface energy, respectively, and W_1 and W_2 represent ‘First Crossover’ and ‘Second Crossover’ of work function. Phase Mismatching and Crossover are given in the last two lines of the table.

x	0%	6%	11%	22%	25%	33%	44%
S_1	10	10	14		∞		14
S_2	19	20			∞		
W_1	5	6	8	22	∞	21	8
W_2	14	16			∞		21
Crossover	9	10	14		∞		14
Phase Mismatching	$4.5 = 9/2-1$	$4 = 10/2-1$	$6 = 14/2-1$		None		$6 = 14/2-1$

**Figure 4.** Second-order derivative of surface energy (a) and work function (b) of HCP $\text{Pb}_{0.75}\text{Bi}_{0.25}$ (0001) films.

$\lambda_{\text{beating}} = \pi / |3k_{\text{BZ}} - 2k_{\text{F}}|$ will increase with doping content. Because bismuth has five valence electrons and lead has four, k_{F} grows bigger along with Bi doping content when $3k_{\text{BZ}} > 2k_{\text{F}}$. In table 4, we list the beating periods of $\text{Pb}_{1-x}\text{Bi}_x$ with different x . As we can see from this table, the beating period indeed increases with x up to 22% doping. Then, surprisingly, perfect bilayer oscillations with infinite beating periods are found both in surface energy and work function at 25% doping concentration, which means that at exactly this doping content, $2k_{\text{F}}$ and $3k_{\text{BZ}}$ are perfectly matched. Figure 4 presents the change of $\Delta^2 E_s(N)$ and work function of HCP $\text{Pb}_{0.75}\text{Bi}_{0.25}$ films in terms of layer numbers. From this figure, we can determine that at positive $\Delta^2 E_s$, which corresponds to a stable layer, local work function has a minimum value. This is in agreement with previous experiments [5, 6, 13]. After 25% Bi content, as more Bi is doped in, the Fermi wave vector keeps on increasing ($3k_{\text{BZ}} < 2k_{\text{F}}$) and the mismatching reappears and increases as Bi content rises. As a result, the beating period decreases from 21 ML to 8 ML, while Bi content increases from 33% to 44%.

To study the phase shift between surface energy and work function, we also list the crossovers of $\Delta^2 E_s(N)$ and work function under different Bi doping contents in table 4. As can be seen in this table, the one additional layer departure from the $\Delta^2 E_s(N)$ phase shift is observed in all types of HCP $\text{Pb}_{1-x}\text{Bi}_x$ (0001) alloy films. As an example, in figure 5, we present the work function and $\Delta^2 E_s(N)$ in HCP $\text{Pb}_{0.56}\text{Bi}_{0.44}$ (0001) films. Under this doping content, the phase shift between $\Delta^2 E_s(N)$ and work function is $(14/2-1)\text{ML}$, while the beating period is 14 ML. At 0%, 6% and 11% Bi doping contents, phase shifts are $(9/2-1)\text{ML}$, $(10/2-1)\text{ML}$ and $(14/2-1)\text{ML}$, respectively, while the beating periods are 9 ML, 10 ML and 14 ML, respectively. Like its FCC partner, phase mismatching between surface energy and work function is $\pi/2 - \delta$ again.

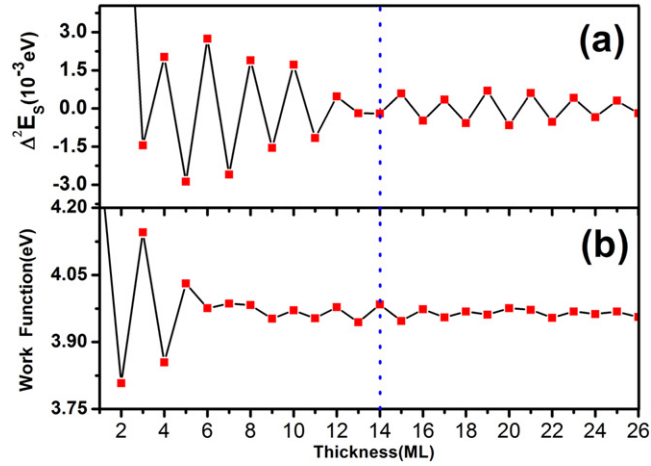


Figure 5. Second-order derivative of surface energy (a) and work function (b) of HCP Pb_{0.56}Bi_{0.44} (0001) films. The dotted line is lined up with adjacent crossovers in $\Delta^2 E_S(N)$ to highlight the phase shift between $\Delta^2 E_S(N)$ and work function.

3.3. Understanding the deviation of phase shift within a free electron model.

From our DFT calculation, we find that in both FCC PbBi (111) and HCP PbBi (0001) alloy films, there are always some extra phase shifts between surface energy and work function, which are usually exhibited as one additional layer shift beyond the $\pi/2$ phase rule. This one-layer departure from the $\pi/2$ phase relation could be well explained within the free electron model with the quantization condition.

As discussed in [4, 24], the oscillation pattern of E_S can be modeled by a damped sinusoidal function,

$$\Delta E_S = \frac{A \sin(2k_F d + \Phi) + C}{d^\alpha}, \quad (2)$$

where k_F is the Fermi wave vector and d is the thickness of the films. An additional phase Φ is introduced to represent the total boundary phase shift caused by vacuum/film interaction [24, 25]. Lattice distortion due to relaxation, which is less than 2% percent on average [22, 24, 26], is neglected here. As we know, the slight departure from the exact matching between Fermi wavelength and lattice space leads to the beating pattern. Since the thickness $d = Nd_0$ can take only integer value N to manifest the beating pattern of surface energy, we can replace the difference wave vector $k_E = \frac{3\pi}{2d_0} - k_F$ with k_F and get the envelope function:

$$\pm \frac{A}{d^\alpha} \sin(2k_E Nd_0 - \Phi) + \frac{C}{d^\alpha}. \quad (3)$$

Here d_0 is the lattice space between two neighbor layers.

As in the vacuum/film interaction leading to the additional phase Φ in surface energy, we can expect that work function will also be affected by this interaction at the interface. Surface energy and work function are connected by a central equation [4]:

$$\frac{1}{d^4} \frac{d}{dd} d^4 E_S = \frac{4E_S}{d} + \frac{d}{dd} E_S = \frac{3}{2} \rho (E_f - E_F). \quad (4)$$

Thus, we can straightforwardly derive the envelope function of work function, which is

$$\mp W_0 \cos(2k_E h - \Phi - \delta) - C', \quad (5)$$

$$\delta = \tan^{-1} \left[\frac{4}{3\pi N} (4 - \alpha) \right], \quad (6)$$

where $W_0 = \frac{2\sqrt{(2k_F A d)^2 + (4 - \alpha)^2}}{3\rho d^{\alpha+1}}$, $C' = \frac{2}{3\rho} \left(\frac{(4 - \alpha)C}{d^\alpha} + \frac{4E_{\infty}}{d} \right)$ and ρ is the electron density. The phase shift between surface energy and work function is perfectly presented in their beating pattern and it will lead the crossovers of work function to be nearly $\pi/2$ (1/4 of a beating period) ahead of the crossovers of surface energy. We can clearly see from equations (3) and (5) that the oscillating parts of ΔE_S and ΔW are sinusoidal and cosine functions, respectively. However, beyond that, the vacuum/film interaction will lead to an extra phase shift δ in the cosine function of the work function. This extra phase will not affect the sign of the work function at normal layers. So, for HCP Pb_{0.75}Bi_{0.25}, where the beating period of surface energy is infinite due to the perfect matching between the Fermi vector and lattice space, this phase shift will not change the sign of the work function at all layers, and

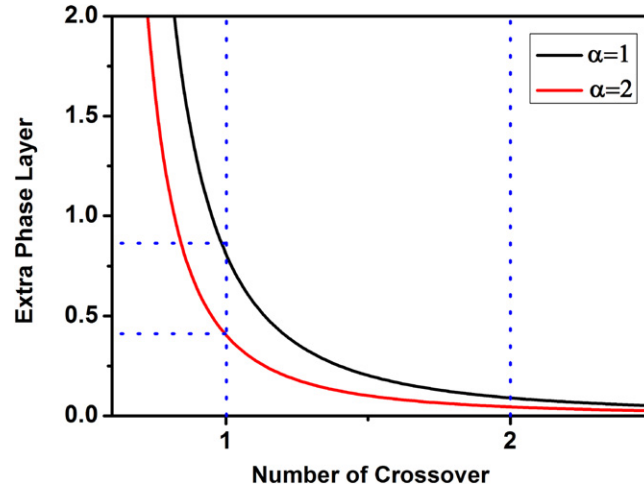


Figure 6. Extra layer shift of work function as a function of the number of crossovers under different decay indexes. The upper line is for $1/d$ decay where $\alpha = 1$, and the lower line is for $1/d^2$ decay where $\alpha = 2$.

thus the beating pattern of work function will also be a perfect bilayer oscillation. But at crossovers of the beating pattern, the value of the cosine function should be zero. Due to the effect of the extra phase δ , the zero value of the cosine function will shift to a higher layer number and thus the appearance of crossovers will be delayed. For different types of $\text{Pb}_{1-x}\text{Bi}_x$ films with different beating periods N_0 , without the extra phase, the $\pi/2$ phase rule will cause crossovers to appear at $N_0 \frac{2n-1}{4}$, where n means the n th crossover. Due to the effect of the extra phase δ , the n th crossover will be postponed by $D = \frac{8(4-\alpha)}{3\pi^2(2n-1)}$ monolayer. As we increase n , the extra layer shift caused by the vacuum/film interaction decays rapidly. This is in agreement with the fact that the effect of vacuum/film interaction diminishes with increasing film thickness and will be less important at large layer numbers.

The decay index is usually assumed to be $\alpha = 2$ in film growth for most of the metal films. However, in the $\text{Pb}(111)$ ultrathin films, the two different Fermi surface sheets along the film growth direction are very flat and the strong nesting of the two Fermi sheets will significantly enhance the charge density oscillations characteristic of a quasi-one-dimensional electron system with a $1/d$ Friedel oscillation decay, thus implying the $\alpha = 1$ decay of both surface energy and work functions [27, 28]. In figure 6, we plot the delay of layers at different crossovers for $\alpha = 1$ and $\alpha = 2$, respectively.

From figure 6 we can see that the delay at the first crossover will be about 0.9 ML if we choose the decay index as $\alpha = 1$. Since the thickness of the layer can only be an integer, this 0.9 ML delay is enough to shift the first crossover for one layer. The most important fact is that D does not depend on the doping concentration, so the delay at the first crossover will always be 0.9 ML for all types of $\text{Pb}_{1-x}\text{Bi}_x$ alloy films, as our results show. This explains the universal existence of one additional layer shift found in all of the doping content of Pb film. Meanwhile, from figure 6, we notice that the additional layer shift indeed decreases rapidly with an increase in layer number. After the second crossover of the work function, the extra phase will be less than 0.1 ML and thus the beating pattern will not be affected at all.

The lower line in figure 6 gives the change of the extra phase when the decay index is $\alpha = 2$. In this case, the vacuum/film interaction will also lead to an extra phase at small layers. However, the extra phase at every crossover is much smaller than when $\alpha = 1$, and thus the one additional layer phase shift cannot appear. So the underlying physical mechanism of this striking one-layer shift is actually tied to the $1/d$ decay for the Friedel oscillation caused by the strong nesting of the two sheets of Fermi surface, which is also the reason for the strong QSEs of PbBi alloy films.

For more clear evidence, we plot $\Delta^2 E_s$ and W as a function of layer numbers obtained from a free electron model in figure 7 for $\text{Pb}(111)$ films. Constants and coefficients are neglected without changing the phase relation. As we can see from this figure, $\Delta^2 E_s$ has a beating behavior with period about 9 ML, which is the same as that shown in table 2. Work function also has a similar beating pattern, except the first crossover of work function is at 5 ML instead of 4 ML. This is because the layer number can choose only an integer number, so the extra phase delay will be manifested as a crossover at 5 ML.

4. Conclusions

In conclusion, by using first-principles calculations, we have investigated the phase relationship between oscillations of surface energy and work function of FCC PbBi(111) and HCP PbBi(0001) ultrathin alloy films.

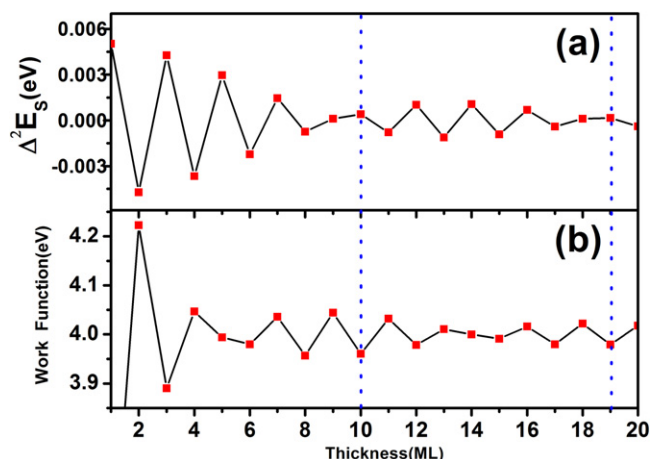


Figure 7. Results from the theoretical calculation for second-order derivatives of surface energy (a) and work function (b) for Pb(111) films. The dotted lines are lined up with adjacent crossovers in $\Delta^2 E_s(N)$ to highlight the phase shift between $\Delta^2 E_s(N)$ and work function.

Many doping contents were chosen in both film types in which the exact phase shift was examined. Different from the previously recognized $\pi/2$ phase shift, we find that there is an additional phase shift δ at small layer numbers. This extra phase shift is caused by the interaction between the vacuum phase and film phase at the surface. As film thickness increases, this interaction becomes less important and the extra phase shift decreases rapidly. Specifically for PbBi FCC(111) and HCP(0001) structures, due to the strong nesting of the two Fermi surface sheets along the film growth direction, the extra phase shift always corresponds to the phase change over one monolayer at the first crossover of work function. Because of the Friedel oscillation in Pb ultrathin films, shown as $1/d$ decay, the Fermi surface sheet is quite flat; thus, the energy attenuation along this direction is very slow. This unique nature provides an opportunity for the appearance of the additional one-layer phase shift. Based on this view, we can predict that other related systems exhibiting flat Fermi surface sheets, such as CoSi2 [29], should also display similar intriguing physical properties. Investigating the phase relationship between oscillations of surface energy and work function is of basic importance in quantum engineering. Such intricate relationships between the surface energy and work function need to be fully explored in future studies.

Acknowledgments

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