ELSEVIER

Surface Science Letters

Growth, stability and morphology evolution of Pb films on Si(1 1 1) prepared at low temperature

Yan-Feng Zhang *, Jin-Feng Jia, Zhe Tang, Tie-Zhu Han,
Xu-Cun Ma, Qi-Kun Xue *

*Beijing National Laboratory for Condensed Matter Physics, Institute of Physics,
The Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, China*

Abstract

Room temperature morphology evolution of Pb thin films, prepared on the Si(1 1 1)-7 × 7 substrate at a low temperature (145 K), is investigated by reflection high energy electron diffraction, scanning tunnelling microscopy and angle-resolved photoemission spectroscopy. A critical thickness of 10 monolayers (ML) is identified, below which all the flat films formed at low temperature are unstable against evolution into interconnected islands at room temperature. From 10 ML to 21 ML, Pb films become stable at room temperature and grow via a bi-layer mode. Above 21 ML, the film growth turns into a layer-by-layer mode. A "beating effect" is observed to modulate this special growth mode, which changes the film stability from even (odd) layers to odd (even) layers with a 9 ML period. Morphology and electronic structure analysis show that the quantum size effect is responsible for the different morphology evolution behaviour and the magic stability of Pb films.
© 2005 Elsevier B.V. All rights reserved.

1. Introduction

Growth of two dimensional (2D) metal films on semiconductor substrates has become a subject of extensive experimental and theoretical studies recently [1]. Due to large lattice mismatch and different chemical bonding nature, to prepare atomically flat metal films on semiconductor substrates remains a great challenge. Recent studies

* Corresponding authors. Tel.: +86 10 8264 9599; fax: +86 10 8264 9228 (Y.-F. Zhang), tel.: +86 10 8264 9561; fax: +86 10 8264 9228 (Q.-K. Xue).
E-mail addresses: yfzhang@aphy.iphy.ac.cn (Y.-F. Zhang), qkxue@aphy.iphy.ac.cn (Q.-K. Xue).

show that a low temperature deposition method could mitigate this problem. With this method, flat metal films had been prepared on several semiconductor substrates, which exhibit an intriguing thickness-dependent stability [2–5]. To understand this special behaviour in thin film growth, an "electronic growth" model was proposed and discussed, where the quantized electrons confined in thin films may play an important role in deciding the film growth [6].

A novel bi-layer growth mode of Pb on Cu(111) was observed back in 1989 with the helium atom scattering (HAS) method [7]. Later on, extensive investigations have been made for studying the quantum size effects (QSE) in Pb, since the Fermi electron wavelength of Pb is nearly four times of the interlayer distance along the (111) direction. As such, the film thickness change by only 1 ML can induce dramatic changes in the electron density of states near the Fermi level [8], and in the physical properties such as magic stability, oscillatory interlayer spacing [9], Hall mobility [10] and superconducting transition temperature [11]. As for the magic stability, most of the previous studies are limited to a low coverage regime, where magic islands of five or seven layers prevail, and this is proved to be closely associated with QSE [12]. Only a few advances have been made in preparing uniform Pb films at even higher coverage [13]. Atomically flat Pb films with a maximum thickness of about 10 ML are successfully prepared by low temperature deposition method, and characterized by formation of diverse quantized energy levels [14]. As the Pb films formed at far from equilibrium conditions are not thermodynamically stable, slight annealing (even warming up to room temperature) could destroy the film uniformity [15]. Therefore, to what extent that QSE can affect the film growth and how stable the films are against thermal annealing are still opening questions.

In this paper, by in situ reflection high energy electron diffraction (RHEED), scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES), we investigated the low temperature growth mode and the thermal stability of Pb films on Si(111) in an extended thickness range (from 6 ML to 24 ML). A critical

thickness of 10 ML for formation of stable flat films at room temperature is identified. Below this thickness, Pb films formed at 145 K are unstable and decay into interconnected islands via void formation and void coalescence during thermal annealing. The film growth proceeds in a quasi bi-layer mode from 10 ML to 21 ML, which can be reasonably explained from an oscillation of the Friedel-typed total energy of this system with a period of about 2 ML. Above 21 ML, the film growth turns into a layer-by-layer mode. A "beating effect" is observed to modulate this special growth mode, which alters the film stability from even (odd) layers to odd (even) layers with a 9 ML period. We show that growth, stability and morphology evolution of Pb films can be understood in terms of QSE.

2. Experimental

Clean Si(111) substrate was prepared by a standard procedure [16]. During Pb deposition in the molecular beam epitaxy (MBE) chamber, the substrate was cooled to about 145 K by a copper block with two liquid nitrogen vessels. The deposition flux of Pb was calibrated by the Pb induced Si(111)-$\sqrt{3} \times \sqrt{3}$ structure and nanostructure array [17]. RHEED patterns were used for real-time monitoring of the film growth and were taken along the $[1\bar{1}0]$ azimuth of the Si(111)-7×7 surfaces at a glancing incidence angle, with an electron beam energy of 12 KeV. After growth, the samples were directly transferred into an ultrahigh vacuum $(5 \times 10^{-11}$ Torr) analysis chamber, where an Omicron STM combined with an ARPES system were installed for in situ surface morphology and electronic structure characterization. The photoemission spectra were collected by a GAMMADATA SCIENTA SES-2002 analyzer, with an energy resolution of 2 meV.

3. Results and discussion

The sharp 7×7 RHEED pattern and the atomically-resolved STM image (not shown) dictate the high crystalline quality of the Si(111)
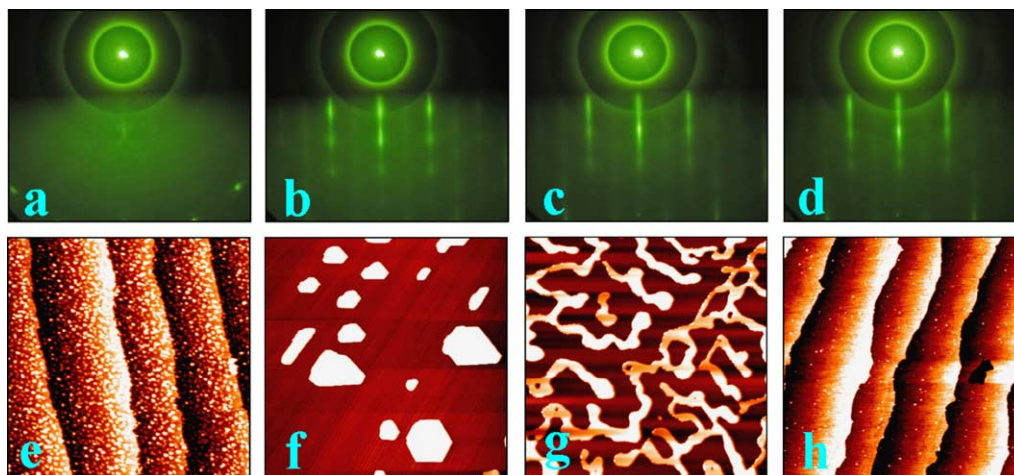
Fig. 1. RHEED patterns ((a)–(d)) taken during Pb deposition on Si(111) kept at 145 K, and the corresponding room temperature STM images ((e)–(h), image size: 2000 nm × 2000 nm). Nominal thicknesses for the Pb films are 1 ML, 3.5 ML, 6 ML and 10 ML for (a)–(d), respectively.

substrate before Pb deposition. The upper panel in Fig. 1 displays the RHHED patterns during Pb deposition for various thicknesses at a substrate temperature of 145 K. We can see that the typical 7× fractional diffraction streaks become weak after 1 ML Pb deposition (Fig. 1(a)), and disappear completely at 1.5 ML (not shown). This corresponds to formation of the well-known featureless wetting layer in this system. With increasing Pb thickness, bright spots superimposing on very dim 1× like streaks appear (Fig. 1(b)), suggesting the formation of 3D islands above the wetting layer. The spots, the fingerprint of the 3D islands, are connected gradually and turn into obvious sharp streaks at a thickness of ∼6 ML (Fig. 1(c)). Above 6 ML, the Pb growth exhibits unique 2D growth character, as shown in Fig. 1(d), where the RHEED pattern of a nominal 10 ML film is shown with a very similar character as that of Fig. 1(c). Usually, extraordinary sharp streaks can be observed in a complete layer (N), with further Pb deposition, less bright spots appear on the streaks, then become intense and diminish until another complete layer (N + 1). Therefore, a layer-by-layer growth mode can be expected above 6 ML. These results are in excellent agreement with a previous real-time X-ray study: A homogeneous wetting layer (1.5 ML thick) forms directly on the

Si substrate and then islands with a fairly uniform height of 5 ML grow on top of the wetting layer, with the film thickness in excess of 6 ML, a nominal layer-by-layer growth follows [18]. This special growth behaviour of Pb is understandable since 2D growth is kinetically accessible due to the decreased atom diffusion at low temperature, as compared with that of the traditional method where 3D growth is thermodynamically promoted.

Usually, annealing facilitates atoms redistribution and improves crystal quality, but what we see here is different. The lower panel in Fig. 1 shows corresponding STM images for the Pb films deposited at low temperature followed with annealing to room temperature. Below 1.5 ML, the featureless wetting layer, consisting of small Pb clusters, is visible in Fig. 1(e), which is in line with the diffraction pattern in Fig. 1(a). Many 3D flat-top islands are observed when the coverage is smaller than 6 ML (see Fig. 1(f)), and they actually originate from the coalescence of the 5 ML islands formed at low temperature and indicated by the streak-plus-spot RHEED pattern in Fig. 1(b). The morphology of the 3D islands is similar with the quantum wedge reported in a previous result, with an average island height of ∼3 nm [8]. Surprisingly, while a uniform film at 6 ML is expected from the RHEED pattern in Fig. 1(c), the corresponding room temperature

STM image indicates a completely different structure: it is characterized by interconnected islands with an average height of ∼3 nm (Fig. 1(g)). Moreover, this situation does not change until the coverage goes up to 10 ML. Interestingly, the Pb films become extremely stable even at room temperature, as consistently shown by the STM image (Fig. 1(h)). Above 10 ML, no change in the RHEED patterns recorded at low temperature and at room temperature is observed, and essentially there is no obvious structure variation in Pb films during the warming up process. Thus, a critical thickness of 10 ML can be identified, which is the lowest thickness for Pb films formed at low temperature to survive at room temperature.

To understand the morphology evolution behaviour below the critical thickness of 10 ML, we took time-dependent RHEED patterns and STM images. As an example, we show the results in Fig. 2 for a film with a nominal thickness of 8 ML. From the RHEED patterns, we can note the sharp pattern characterizing formation of flat film at low temperature (Fig. 2(a)) change into spot-plus-streak patterns gradually as the substrate temperature is increased (Fig. 2(b)–(d)). A more visual morphology evolution comes from the STM observations: when the substrate temperature reaches 200 K, from Fig. 2(e) we can see that

the film involve one and two atomic layer islands, as well as some hexagonal voids down to the wetting layer (these voids can be used to measure the apparent height of the Pb film). As a rule, the film increases its thickness always at the expense of void formation and void growth, as required by mass conservation (Fig. 2(f)). With increasing substrate temperature (Fig. 2(g)), the original film continues to evolve and finally decay into interconnected islands at room temperature (Fig. 2(h)). Thus, the voids down to the wetting layer can be regarded as seeds for the 2D–3D morphology transition. We also find that a film with a thickness closer to the critical thickness takes longer time to reach the final interconnected islands morphology. Similar results have been reported in the Ag/GaAs(110) system previously [19,20].

The above morphology evolution can be well explained in terms of the ''electronic growth'' model. According to this model, the stability of a thin film is closely related to the electronic contribution to the system total energy, which mediates a long-range force, counteracting the unfavorable over-layer substrate interface energy [6]. For thin films prepared at a low temperature of 145 K, the system is usually trapped in a metastable state with a local energy minimum. For Pb, this special film thickness may be 6 ML [18]. The surface
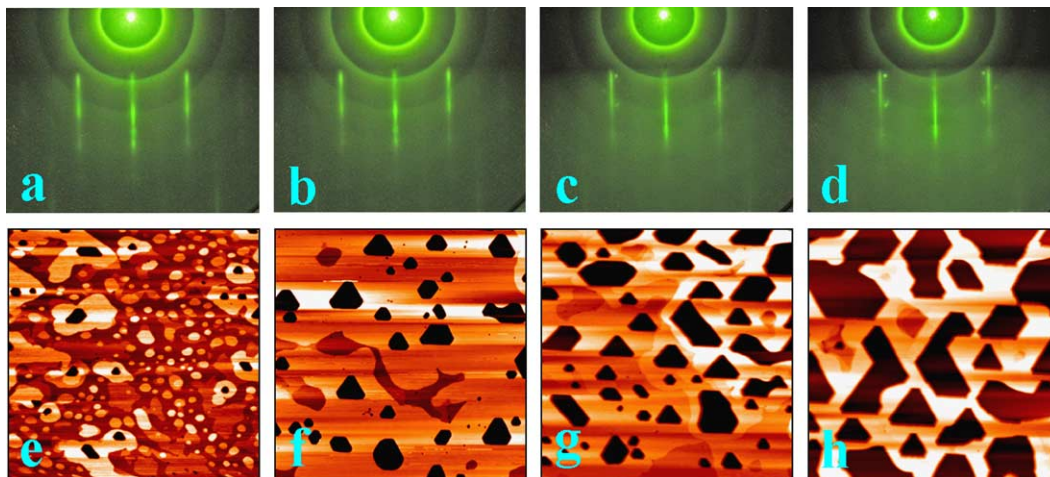

Fig. 2. Time-elapsing RHEED patterns ((a)–(d)) and corresponding STM images ((e)–(h), image size 1000 nm × 1000 nm) for a nominal 8 ML Pb film with the substrate temperature kept at 200 K, 220 K, 250 K and 270 K, respectively. The hexagonal structures are the void islands down to the wetting layer.

energy calculations reveal that the system energy always decays with increasing film thickness [15,18]. In a low thickness regime (from 6 ML to 10 ML), annealing can provide a special kinetic pathway or enough thermal energy to drive the system away from the local energy minimum and develop towards a broader energy landscape, thus a roughing of the film takes place. At room temperature, the system can be trapped in another energy minimum, and the preferred thickness turns out to be 10 ML. Compared with the Pb films deposited on the Pb/Si(1 1 1)-($\sqrt{3} \times \sqrt{3}$) substrate, a 11 ML film can break up before room temperature and evolve into interconnected islands finally. The discrepancy indicates that the buried interface may play a crucial role in stabilizing the Pb films. Similar results can be acquired from the different island growth behaviour of Pb on Si(1 1 1), seen at low temperature deposition with different interface structures [12]. Otherwise, for metallic films deposited on semiconductor surfaces with a large thermal expansion misfit, the stress effect may be another factor that influences the stability of Pb films prepared at low temperature followed with annealing [21].

At 10 ML, since uniform Pb films can be prepared and be stable at room temperature, the subsequent growth should behave essentially a homoepitaxy of Pb/Pb(1 1 1), and a layer-by-layer growth mode is expected, as we previously observed in the Al/Si(1 1 1) system [5]. This was indeed observed in our experiment, but the film growth proceeds via a layer-by-layer or a bi-layer mode. Fig. 3 shows two typical STM images, which illustrate this special growth mode clearly. For a film with a nominal thickness of 12.2 ML shown in Fig. 3(a), the corresponding line profile indicates that the additional 0.2 ML Pb forms one atomic layer high islands on the underlying Pb terraces. This implies that there is a layer-by-layer growth trend from 12 ML to 13 ML, and a delicate illustration of this special point can be seen in the rear part of the paper. In the case of a 15.6 ML film (Fig. 3(b)), the line profile below shows that the islands are actually two-atomic-layer high. Additional Pb deposition with a total thickness up to an integer layer always results in uniform films (seen in Fig. 3(c) and (d)). We can

notice while flat films could be prepared in this thickness regime, the system exhibit intriguing oscillatory stable character with a period of 2 ML.

As we cannot only use STM to acquire definite values of the film thicknesses, determination the magic stability in Pb layers demands a more sensitive tool for absolute film thickness characterization. Photoemission spectroscopy probes the quantized energy levels in a thin film, which can be used to measure indirectly the film thickness by a Bohr–Sommerfeld quantization rule, as reported in previous studies [22]. We perform photoemission measurements for different layers with film thicknesses above 10 ML, and the results are displayed in Fig. 4 (The morphology of these layers was also characterized by STM). The sharp and intense peaks near the Fermi level correspond to the quantum well sates (QWS), while the broad and less intense peaks with a binding energy more than 0.5 eV are from the resonance states (or QWS in general). Evidently, if a film is terminated with a complete layer, its spectra will have only one set of QWS with intense and sharp peaks. Such kind of spectra appears in the stable films with thicknesses of 10 ML, 12 ML, 13 ML, 15 ML, 17 ML, 19 ML and 21 ML–24 ML. However, for the films with nominal thicknesses of 11 ML, 14 ML, 16 ML, 18 ML and 20 ML, half of the surface is covered by 2 ML islands (as reconfirmed by the STM observation), and the corresponding photoemission spectra exhibit a mixture from the adjacent stable layers (Fig. 4). For example, in the spectrum of an 18 ML film, the binding energy of the QWS locates in between that of the QWS for 17 ML and 19 ML. From these observations, a bi-layer growth mode can be deduced below 21 ML with a turning point at 13 ML, where the stable thicknesses transfer from even layers (below 13 ML) to odd layers. Above 21 ML, Pb growth proceeds via a quasi layer-by-layer mode and continuous layers can be obtained in this thickness regime (seen in Fig. 4). As for the identification of the turn-around point, this can be clearly identified from the spectrum of a 12.4 ML film, which possess the character spectra from both even (12 ML) and odd (13 ML) layers. At the same time, we note that the film thickness fluctuation by only 0.3 ML can break down the singularity of the peaks of QWS,
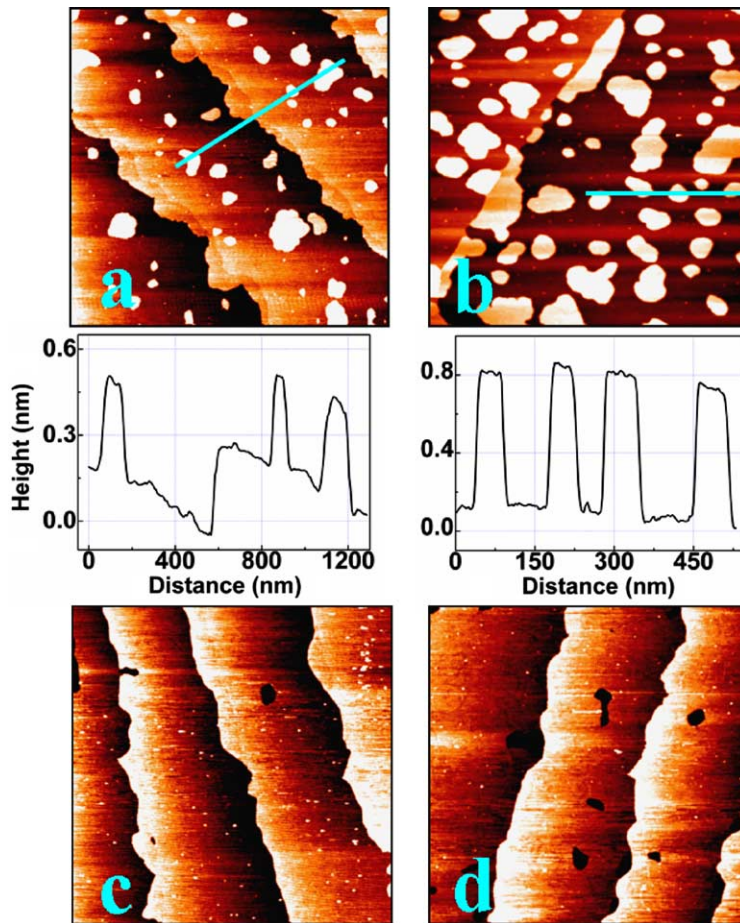
Fig. 3. STM images obtained from Pb films with a nominal thickness of (a) 12.2 ML (2000 nm × 2000 nm) and (b) 15.6 ML (1000 nm × 1000 nm), illustrating the layer-by-layer or bi-layer growth mode. The line profiles of the images in (a) and (b) clearly reveals that the islands above the complete film are 1 ML or 2 ML high. Room temperature deposition of additional 0.8 ML Pb in (a) and 1.4 ML Pb in (b) result in almost perfect films, and corresponding STM images are displayed in (c) and (d).

as also can be seen from the spectra of other incomplete films (21.3 ML and 22.4 ML).

In a recent well-executed experiment [23], Ag films on Fe(1 0 0) substrate with magic film thicknesses of 1 ML, 2 ML and 5 ML are discussed to be stable up to 800 K, and the electron quantized energy levels or QWS associated with a known film thickness was proved to account for this magic stability. Theoretically, the stability analysis of a system is usually based on the total electronic energy calculation, which should contain all the occupied states below the Fermi level within the first surface Brillouin zone. The energy difference between two layers can be described as

$$\Delta E(N) = \frac{1}{2}\left[E(N+1) + E(N-1)\right] - E(N)$$

where a large positive $\Delta E(N)$ corresponds to a stable film.

From our experimental photoemission spectra (Fig. 4), we know that as the film thickness (N) increases by 2 ML, a new branch of QWS crosses the Fermi level and becomes occupied, as also predicted in a theoretical result before [24]. Thus, the peaks of the highest occupied QWS oscillate relative to the Fermi level with a period of one half of the Fermi wavelength (~2 ML), and the whole electronic energy below the Fermi level oscillates
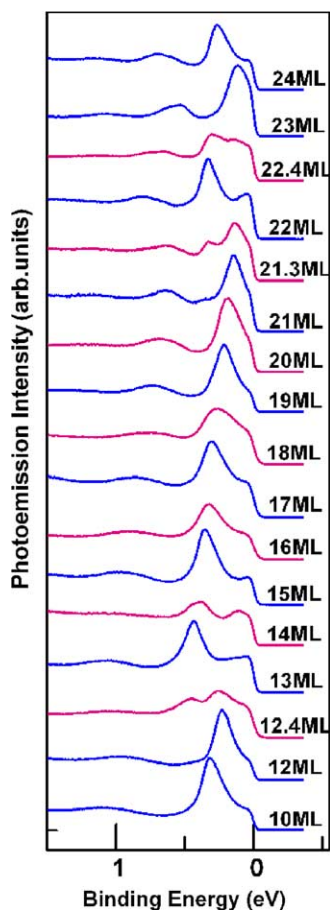
Fig. 4. Normal emission spectra of the Pb films (from 10 ML to 24 ML) collected at a substrate temperature of 110 K. Successive spectra are graphically offset for clarity. The Fermi level corresponds to 0 eV binding energy.

layers becomes less obvious, and similar stability can be anticipated in this case, then a layer-by-layer growth mode follows.

Moreover, as the film thickness in terms of atomic layer must be an integer, the mismatch between 2 ML period of film stability and 1.8 ML (one half of the Fermi wavelength) should give rise to a "beating effect" with a 9 ML period, as discussed in previous theoretical calculations before [15,18]. In our experiment, this "beating effect" can be clearly observed in the photoemission data of Pb films at 13 ML and 22 ML. An increase of the quantum well width by 1 ML (from 12 ML to 13 ML, and from 21 ML to 22 ML) will cause a new state drop right below the Fermi level, which is unusually far away from the Fermi level in contrast with other adjacent thicknesses. At these points, the stability of the Pb films switches from even (odd) layers to odd (even) layers. Although the magic stability of Pb films with a maximum thickness of 25 ML has been investigated theoretically from the surface energy [24] and the electron total energy calculations before [25], the present study provides experimental proof for the influence of QSE on film growth over a more wide thickness range, using a different kinetic pathway to prepare atomically flat Pb films at low temperature followed with annealing to room temperature.

4. Summary

Low temperature growth and thermal stability of Pb films on Si(1 1 1) are investigated systematically by RHEED, STM and ARPES. At a low temperature deposition condition (145 K), flat Pb films start to form at a thickness of 6 ML, and then the film growth follows with a layer-by-layer mode. Therefore, 6 ML is the lowest coverage for formation of complete Pb film at low temperature.

When Pb films prepared with low temperature deposition are annealed to room temperature, dramatic changes of the film morphology occur as a function of film thickness. With film thickness range from 6 ML to 10 ML, the system become unstable and decay into interconnected islands at room temperature. Above 10 ML, Pb films grow via a bi-layer mode and exhibit an oscillatory

with the same period correspondingly. In the low thickness regime, the QWS are largely spaced, where the energy difference between adjacent even and odd layers is obvious. For a Pb film with a thickness of N atomic layers, if its highest occupied QWS is very close to the Fermi level, the film is less stable compared with the neighboring layers. A small perturbation, for example by thermal annealing, will drive the unstable film bifurcate into stable layers ($N \pm 1$) to minimize the system energy. This explains the bi-layer growth mode for the films from 10 ML to 21 ML prepared at low temperature followed with annealing. In a higher thickness regime, the energy difference between two adjacent

stability with a period of 2 ML. A beating effect is also observed, where the relative stability of the Pb films alters from even (odd) layers to odd (even) layers with a 9 ML period. Otherwise, ARPES study clearly shows that all the stable films are characterized with well-defined QWS, where the electron energies of the quantum wells exhibit a Friedel-typed oscillation with a small period of 2 ML and a modulatory "beating effect" of a 9 ML period. This oscillation in electron total energy is expected to responsible for the magic stability and the novel growth behaviour of Pb on Si(1 1 1), and is actually a reflection of QSE. Depending on the thickness-dependent analysis of the QWS in Pb films over a wide thickness range, we have also studied the band structure of Pb under a phase accumulation model and will report it elsewhere [26].

Acknowledgement

References

[1] V.A. Grazhulis, Prog. Surf. Sci. 36 (1991) 89;
W.G. Schmidt, F. Bechstedt, G.P. Srivastava, Surf. Sci. Rep. 25 (1996) 141.

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

[3] L. Huang, S. Jay Chey, J.H. Weaver, Surf. Sci. 416 (1998) L1101;
L. Gavioli, K.R. Kimberlin, M.C. Tringides, J.F. Wendelken, Z.Y. Zhang, Phys. Rev. Lett. 82 (1999) 129.

[4] C.-S. Jiang, H.B. Yu, C.-K. Shih, Ph. Ebert, Surf. Sci. 518 (2002) 63.

[5] H. Liu, Y.F. Zhang, D.Y. Wang, M.H. Pan, J.F. Jia, Q.K. Xue, Surf. Sci. 571 (2004) 5;
Z.Y. Zhang, Surf. Sci. 571 (2004) 1.

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

[7] B.J. Hinch, C. Koziol, J.P. Toennies, G. Zhang, Europhys. Lett. 10 (1989) 341;
B.J. Hinch, C. Koziol, J.P. Toennies, G. Zhang, Vacuum 42 (1991) 309.

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

[9] P. Czoschke, H. Hong, L. Basile, T.-C. Chiang, Phys. Rev. Lett. 91 (2003) 226801.

[10] I. Vilfan, M. Henzler, O. Pfennigstorf, H. Pfnür, Phys. Rev. B 66 (2002) 241306.

[11] Y. Guo, Y.F. Zhang, X.Y. Bao, T.Z. Han, Z. Tang, L.X. Zhang, W.G. Zhu, E.G. Wang, Q. Niu, Z.Q. Qiu, J.F. Jia, Z.X. Zhao, Q.K. Xue, Science 306 (2004) 1915.

[12] K. Budde, E. Abram, V. Yeh, M.C. Tringides, Phys. Rev. B 61 (2000) R10602;
V. Yeh, L. Berbil-Bautista, C.Z. Wang, K.M. Ho, M.C. Tringides, Phys. Rev. Lett. 85 (2000) 5158;
W.B. Su, S.H. Chang, W.B. Jian, C.S. Chang, L.J. Chen, T.T. Tsong, Phys. Rev. Lett. 86 (2001) 5116;
M. Hupalo, M.C. Tringides, Phys. Rev. B 65 (2002) 115406.

[13] A. Mans, J.H. Dil, A.R.H.F. Ettema, H.H. Weitering, Phys. Rev. B 66 (2002) 195410.

[14] M.H. Upton, C.M. Wei, M.Y. Chou, T. Miller, T.-C. Chiang, Phys. Rev. Lett. 93 (2004) 026802.

[15] P. Czoschke, H. Hong, L. Basile, T.-C. Chiang, Phys. Rev. Lett. 93 (2004) 036103.

[16] J.-L. Li, J.-F. Jia, X.-J. Liang, X. Liu, J.-Z. Wang, Q.-K. Xue, Z.-Q. Li, J.S. Tse, Z.Y. Zhang, S.B. Zhang, Phys. Rev. Lett. 88 (2002) 066101.

[17] S.-C. Li, J.-F. Jia, R.-F. Dou, Q.-K. Xue, I.G. Batyrev, S.B. Zhang, Phys. Rev. Lett. 93 (2004) 116103.

[18] H. Hong, C.-M. Wei, M.Y. Chou, Z. Wu, L. Basile, H. Chen, M. Holt, T.-C. Chiang, Phys. Rev. Lett. 90 (2003) 076104.

[19] M.M.R. Evans, B.Y. Han, J.H. Weaver, Surf. Sci. 465 (2000) 90.

[20] H.B. Yu, C.S. Jiang, Ph. Ebert, X.D. Wang, J.M. White, Q. Niu, Z.Y. Zhang, C.K. Shih, Phys. Rev. Lett. 88 (2002) 016102.

[21] Z.G. Suo, Z.Y. Zhang, Phys. Rev. B 58 (1998) 5116.

[22] T.-C. Chiang, Surf. Sci. Rep. 39 (2000) 181.

[23] D.-A. Luh, T. Miller, J.J. Paggel, M.Y. Chou, T.-C. Chiang, Science 292 (2001) 1131.

[24] C.-M. Wei, M.Y. Chou, Phys. Rev. B 66 (2002) 233408.

[25] G. Materzanini, P. Saalfrank, P.J.D. Lindan, Phys. Rev. B 63 (2001) 235405.

[26] Y.F. Zhang, J.F. Jia, T.Z. Han, Z. Tang, Q.T. Shen, Y. Guo, Z.Q. Qiu, Q.K. Xue, Phys. Rev. Lett. 95 (2005) 096802.