

# Van Hove Singularities as a Result of Quantum Confinement: The Origin of Intriguing Physical Properties in Pb Thin Films

Yu Jie Sun<sup>1,2</sup>, S. Souma<sup>2</sup>, Wen Juan Li<sup>3</sup>, T. Sato<sup>4</sup>, Xie Gang Zhu<sup>1</sup>, Guang Wang<sup>1</sup>, Xi Chen<sup>1</sup>, Xu Cun Ma<sup>3</sup>, Qi Kun Xue<sup>1,2,3</sup>, Jin Feng Jia<sup>1</sup> (✉), T. Takahashi<sup>2,4</sup>, and T. Sakurai<sup>2</sup>

<sup>1</sup> Key Laboratory of Atomic and Nanosciences, Department of Physics, Tsinghua University, Beijing 100084, China

<sup>2</sup> WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

<sup>3</sup> Institute of Physics, The Chinese Academy of Sciences, Beijing 100190, China

<sup>4</sup> Department of Physics, Tohoku University, Sendai 980-8578, Japan

Received: 13 August 2010 / Revised: 14 September 2010 / Accepted: 14 September 2010

© The Author(s) 2010. This article is published with open access at Springerlink.com

## ABSTRACT

*In situ* angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling spectroscopy (STS) have been used to study the electronic structure of Pb thin films grown on a Si(111) substrates. The experiments reveal that the electronic structure near the Fermi energy is dominated by a set of m-shaped subbands because of strong quantum confinement in the films, and the tops of the m-shaped subbands form an intriguing ring-like Van Hove singularity. Combined with theoretical calculations, we show that it is the Van Hove singularity that leads to an extremely high density of states near the Fermi energy and the recently reported strong oscillations (with a period of two monolayers) in various properties of Pb films.

## KEYWORDS

Van Hove singularity, angle-resolved photoemission spectroscopy (ARPES), scanning tunneling spectroscopy (STS), Pb film

## 1. Introduction

Atomically flat metal thin films grown on a semiconductor or an insulator substrate provide an ideal system to study the “particle-in-a-box” problem [1]. When the thickness of such metal films is small and comparable to the wavelength of electrons at the Fermi energy, quantized electronic states, known as quantum well states (QWSs), will form. The physical and chemical properties of the films are expected to be strongly thickness-dependent due to quantum size effects. Indeed, thickness-dependent quantum oscillations have been reported for a variety of

properties of different two-dimensional (2-D) metal films, e.g., resistivity of Au films [2], and stability [3] and work function [4] of Ag films. For most metals, the wavelength of electrons is on the nanometer scale, and therefore significant quantum size effects (QSE) occur in the small thickness regime, usually at a thickness less than 10 monolayers (ML) [2–4]. In this regard, Pb thin films represent a peculiar system. In this system, quantum size effects have been observed to drive quantum oscillation of many properties with a period of 2 ML: examples include the superconducting transition temperature  $T_c$  [5–6], thermal stability [11], thermal expansion coefficient [12], electron–phonon

Address correspondence to jjf@tsinghua.edu.cn

coupling [13], local work function [14], surface reactivity [15] and Kondo effect [16]. These have been explained by an oscillation in electronic density of states (DOS) near the Fermi level ( $E_F$ ) [5–17], particularly in the bottom of subbands that pass through the Fermi level [18, 19]. More interestingly, the oscillations in the properties of Pb persist for large film thicknesses, and quantized electronic states have even been observed at film thicknesses up to 45 ML [14], a much larger thickness [5–17] than observed for other films [2–4]. These strong oscillations in the properties of thick Pb films are very puzzling since, according to theory, the quantum size effect should quickly become damped with increasing thickness [18]. The electronic structure of Pb films with different thicknesses has been studied by photoemission spectroscopy and scanning tunneling spectroscopy (STS) [5, 12, 14–16]. Many of these studies have revealed that the oscillations in the DOS at  $E_F$  are consistent with the observed properties of the films—for instance, higher superconducting transition temperature ( $T_c$ ) [5], surface reactivity [15] and Kondo temperature [16]. However, why the Pb films exhibit much stronger DOS oscillations than other 2-D systems is still an open question.

In this paper, we report the results of angle-resolved photoemission spectroscopy (ARPES) and STS on Pb/Si(111) films. By comparing ARPES and STS, we found that “extended” Van Hove singularities (VHSs) observed by ARPES measurements correspond to the peaks in STS, indicating the extremely high DOS. On the basis of our measurements, we also discuss the origin of the strong oscillations in the properties of Pb films.

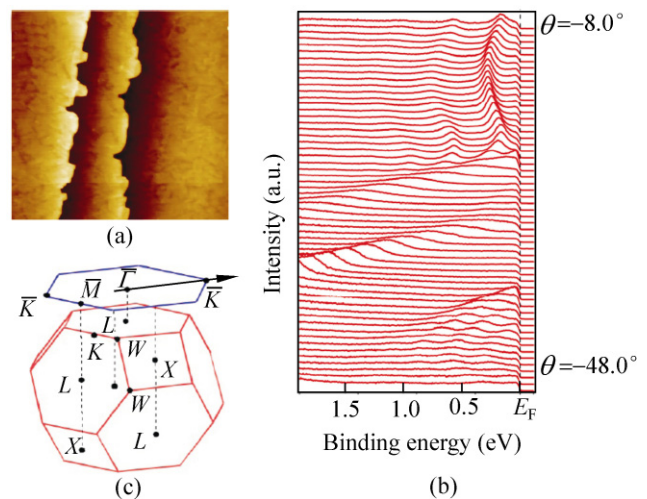
## 2. Experimental

Our experiments were performed in an ultra-high vacuum molecular beam epitaxy–STM–ARPES combination system (Omicron), which allowed us to define the thickness of a Pb film precisely and measure the electronic structure by STS and ARPES on a given sample *in situ*. The base pressure of the system was better than  $5 \times 10^{-11}$  Torr. Atomically flat Pb films were prepared by a low temperature deposition method on Si(111)- $7 \times 7$  surfaces. Details of the sample

preparation have been described elsewhere [20]. The STS measurements were conducted at 4.2 K, while the photoemission spectra were collected by a Gamamata Scienta R4000 analyzer at 15 K in the same chamber. We used the HeI (21.218 eV) resonance line to excite photoelectrons. The energy resolution and angular resolution were set at 10 meV and 0.2 degrees, respectively.

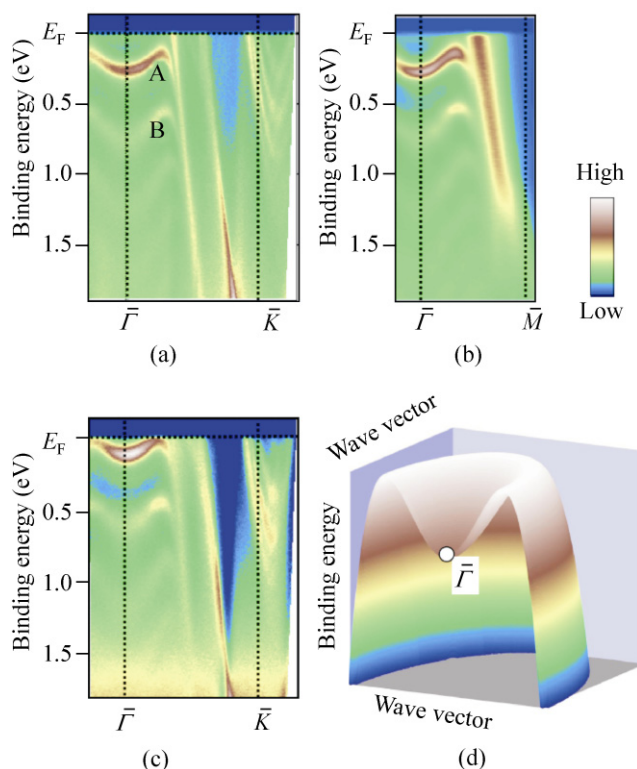
## 3. Results and discussion

A typical STM image of an atomically flat Pb film with a thickness of 24 ML is shown in Fig. 1(a). The ARPES spectra along the  $\bar{\Gamma}\bar{M}$  direction of the film are shown in Fig. 1(b), and the corresponding ARPES intensity map plot as a function of binding energy and wave vector is displayed in Fig. 2(a). The color-coded (white–brown–yellow) areas correspond to experimentally determined band dispersion. Near the  $\bar{\Gamma}$  point, we can clearly observe several parabolic bands. Their similar dispersion behavior indicates that they are quantum well states. The first subband below  $E_F$  (defined as band A) is located at 0.27 eV at the  $\bar{\Gamma}$  point, while the second one (band B) is at 0.72 eV. In other 2-D systems (e.g., Ag and Cu films)



**Figure 1** (a) Scanning tunneling microscopy image ( $500 \text{ nm} \times 500 \text{ nm}$ ) of a 24 ML Pb film. (b) Angle-resolved photoemission spectra along the  $\bar{\Gamma}\bar{K}$  direction from the same film shown in (a), measured at 15 K from  $\theta = -8.0^\circ$  to  $48.0^\circ$ .  $\theta$  is the emission angle relative to the surface normal. The photon energy used was 21.218 eV. (c) The bulk Brillouin zone of bulk Pb and the corresponding surface Brillouin Pb/Si (111)

[21, 22], the QWSs are free-electron-like and cross the Fermi level. The subbands near the  $\bar{\Gamma}$  point bend to higher binding energy (band A starts bending at an energy of 0.15 eV while band B starts bending at 0.56 eV). We call these subbands “m-shaped” bands. The band bending, which deviates from free-electron dispersion in the “particle-in-a-box” model, is noteworthy because it induces unconventional physical properties in the Pb films, as discussed later. In the middle path from the  $\bar{\Gamma}$  to the  $\bar{K}$  point, a series of steep bands cross  $E_F$ , indicating the metallic nature of the film. The m-shaped dispersion of the QWSs of the 24 ML film is also observed in thinner films [23–25]. However, coupling with the silicon valence band, which occurs in thinner Pb films, is not observed here. With increasing wave vector (close to the  $\bar{K}$  point), we can observe other three parabolic bands in an energy range from  $E_F$  to 1 eV.



**Figure 2** Energy bands measured along the (a)  $\bar{\Gamma}\bar{K}$  and (b)  $\bar{\Gamma}\bar{M}$  direction for a 24 ML film. (c) Energy bands for a 23 ML film along the  $\bar{\Gamma}\bar{K}$  direction. During the measurements, the sample temperature was set at 15 K. (d) Schematic drawing of an m-shaped band in 3-D view, in which a crater-like structure from band bending is clearly seen

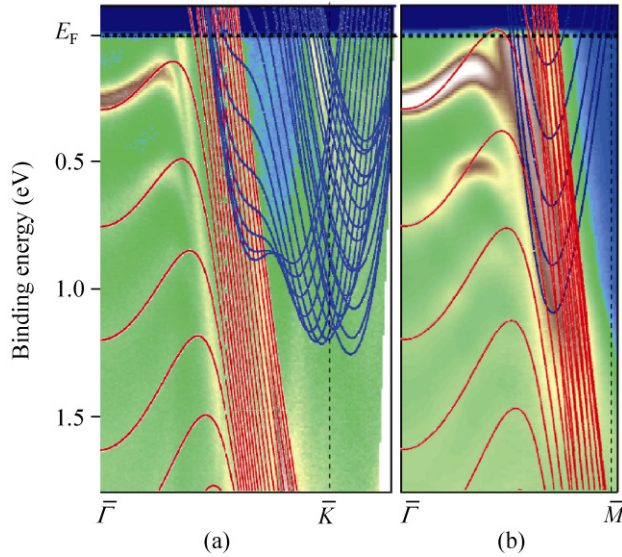
The free-electron-like and bending-back dispersions are also observed in the  $\bar{\Gamma}$  direction, as shown in Fig. 2(b). The m-shaped bands only show a slightly anisotropic behavior: band A bends at 0.14 eV while band B at 0.53 eV; these values are 10 meV and 30 meV higher than the corresponding values in the  $\bar{\Gamma}\bar{K}$  direction, respectively. In contrast to the  $\bar{K}$  point, QWS is not observed at the  $\bar{M}$  point. A 23 ML film shows a noticeable change in electronic structure, but band bending is also observed. The binding energy of the first QWS below the Fermi energy is 0.13 eV at the  $\bar{\Gamma}$  point and bends at 0.02 eV, while the second one shifts to 0.63 eV at the  $\bar{\Gamma}$  point and bends back at 0.47 eV. The difference for other bands (steep and parabolic bands near the  $\bar{K}$  point) is not as evident as for the m-shaped bands because of their high density in  $k$ -space (see the upper right parts of Figs. 2(a) and 2(b)).

To understand the origin of the band bending behavior, we calculated the band dispersions of 23 and 24 ML Pb films. The bands of bulk Pb were calculated by using the orthogonal plane wave (OPW) method [26]. According to the phase accumulation model [1], these bands are quantized in Pb films due to QSE. As a result, the QWSs in a film satisfy

$$\phi_B + \phi_C + 2k_z(E)d = 2\pi n \quad n = (1, 2, 3, \dots) \quad (1)$$

where  $\phi_B$  and  $\phi_C$  are the phase shift at the surface and the interface between the Pb film and the Si substrate, respectively,  $k_z(E)$  is the wave vector in the direction perpendicular to the surface (i.e., along the  $\Gamma L$  direction of the bulk),  $d$  is the film thickness, and  $n$  is the quantum number of the QWS. Although the phase shift is generally a function of  $E$  and  $k$ , a linear phase shift dependence on energy ( $E$ ) was used here for simplicity of calculation. The detailed energy-dependent phase shift was fitted by the energies of the QWSs of a 24 ML Pb film at the  $\bar{\Gamma}$  point. The dispersion of Pb films was calculated using the same phase shift and the band structure of bulk Pb. The calculated bands, which are shown as red and blue lines in Fig. 3(a), are consistent with the experimental data. The m-shaped bands and the steep bands (red lines) are derived from the same band ( $p_z$ ) in bulk Pb. In other words, the steep bands are also m-shaped, but their free-electron-like parts are located well above  $E_F$  and cannot be seen

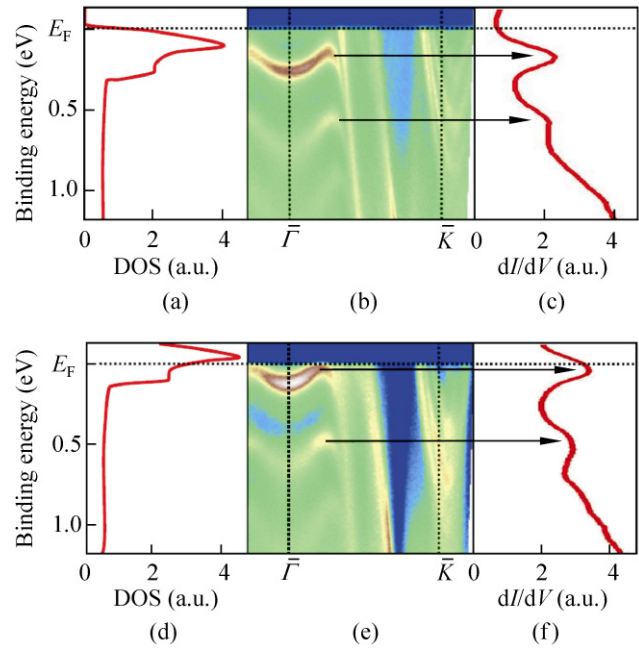




**Figure 3** Comparison between the experimental band dispersion and theoretical calculations for a 24 ML Pb film along the (a)  $\bar{\Gamma}\bar{K}$  and (b)  $\bar{\Gamma}\bar{M}$  direction. The red and blue lines correspond to calculated  $p_z$  and  $p_{xy}$  QWSs, respectively

here. However, the newly observed parabolic bands ( $p_{xy}$ , blue lines) originate from another band of bulk Pb. We also display the simulated band structure in the  $\bar{\Gamma}\bar{M}$  direction (Fig. 3(b)). The deviation from the ARPES measurements is 0.1–0.2 eV, larger than in the  $\bar{\Gamma}\bar{K}$  direction. This difference could be induced by the phase accumulation model [1], and  $k$ -independent phase shift parameters. The effective masses of calculated subbands near the  $\bar{\Gamma}$  point are significantly smaller than those of the observed QWSs. As a result, the tops of the m-shaped bands have lower binding energies.

The electronic DOS near  $E_F$  largely determines the physical properties of a material. To analyze the DOS distribution in Pb films, we carried out STS ( $dI/dV$ ) measurements on 24 ML (Fig. 4(c)) and 23 ML (Fig. 4(f)) Pb films, and directly compared the results with the ARPES spectra (along the  $\bar{\Gamma}\bar{K}$  direction). Quantized QWSs are clearly observed in STS, and these give rise to the high DOS in the films. We know that the bottoms of the m-shaped bands near the  $\bar{\Gamma}$  point in the ARPES measurements correspond to the energy positions of the peaks in the normal emission experiment [5]. However, the high DOS regions (the peaks) in STS do not match the band bottoms but, rather, the tops where the m-shaped bands start bending to higher binding



**Figure 4** (a) Calculated DOS of the first QWS below  $E_F$ , (b) ARPES and (c) STS spectra (measured at 4.2 K) of a 24 ML Pb film. (d) Calculated DOS of the first QWS below  $E_F$ , (e) ARPES and (f) STS spectra of a 23 ML Pb film

energies, as shown by the arrows in Fig. 4. The correspondence between STS and ARPES measurements suggests that the tops of the m-shaped bands contribute greatly to the DOS in the Pb films. Since the DOS of a two-dimensional band is proportional to  $dk_x \cdot dk_y / dE$ , where  $k_x$  and  $k_y$  are wave vectors of two directions and  $E$  is energy, we can obtain the theoretical DOS distribution. For comparison, the theoretical DOS distribution of the first m-shaped band is plotted in Fig. 4(a) for 24 ML and Fig. 4(d) for 23 ML, respectively. In the case of 24 ML, the DOS remains at a very low constant value from 1.8 to 0.28 eV. This DOS is from the steep part of the band due to the 2-D nature of the free-electron-like band. At 0.27 eV, the DOS exhibits a sharp step, which is from the parabolic part of the m-shaped band near the  $\bar{\Gamma}$  point. Like the steep part, the parabolic part also makes a contribution to an energy-independent DOS from 0.28 eV to 0.24 eV. The DOS increases much more rapidly after 0.24 eV, where the band deviates from free-electron-like. A pronounced DOS peak appears at 0.11 eV, consistent with the peak in STS. It is noted that there is a small difference ( $\sim 50$  meV) between experiment and theory.

This is due to the oversimplified model that leads to a lower binding energy for the top of the m-shaped band along the  $\bar{\Gamma}\bar{M}$  direction: the theoretical binding energy of the band top in  $\bar{\Gamma}\bar{M}$  is six times larger than the experimental data. The deviation not only decreases the binding energy of the DOS peak, but also strongly enhances the anisotropy of the m-shaped bands. We also found that the anisotropy of the top is also important in terms of the DOS: lower differences correspond to higher DOS, as well as higher peaks in STS, such as band A and band B in 24 ML Pb films. Therefore, it is expected that the top of the m-shaped band should produce a much higher DOS peak than the calculation. A similar relationship between ARPES and STS data is also observed for the 23 ML Pb film, as shown in Figs. 4(d) and 4(e).

It is now clear that a singularity in DOS near  $E_F$  develops from the top of the m-shaped band due to band bending. This singularity can be well understood in terms of the 2-D nature of the band. Although the bottom of the band at the  $\bar{\Gamma}$  point, e.g., the first QWS with a binding energy of 0.28 eV in the 24 ML film, is an M0 type VHS of 2-D [27, 28], the parabolic part only displays a finite constant DOS. Obviously, such a type of DOS cannot significantly change the properties of a thin film because there are many bands crossing  $E_F$  in such a thick film. On the other hand, the 2-D m-shaped band bends along any direction in the Brillouin zone at almost the same binding energy, forming a crater-like band structure (see the 3-D view in Fig. 2(d)). The situation leads to a characteristic ring of VHSs and an infinite singularity in DOS near  $E_F$ .

As far as we know, this is a new kind of infinite critical point, which is different from the well-known M1 singularity with a single saddle point [27, 28]. Assuming an isotropic band, the angle-independent band dispersion near the VHSs can be expressed by the second-order approximation with polar coordinates

$$E(k, \theta) = E_c + C(k - k_c)^2 + \dots \quad (2)$$

where  $E_c$  and  $k_c$  are the energy and wave vector of the critical points, respectively, and  $C$  is a constant. We can easily obtain the DOS near the singularities

$$g(E) \propto k_c (E - E_c)^{-1/2} \quad (3)$$

which is much larger than that at the saddle point,

$\ln(E - E_c)$  [27, 28], and can be as large as the VHS in a one dimensional (1-D) system [27]. This is the reason why the STS of Pb films display a series of peaks [10] like a 1-D system [29], which has not been observed in any other 2-D system. The QWSs around the  $\bar{K}$  point do not show an evident relationship with the DOS because they always cross the Fermi level very steeply. As a consequence, they give rise to a relatively constant DOS.

The m-shaped band originates from the band structure of bulk Pb: for a particular  $k_x$ , the  $p_z$  band of the bulk is m-shaped. Because the phase shift is not very high, the quantized bands show a similar dispersion behavior in the Pb film, forming the DOS singularity. This is an important reason why we believe that a similar VHS exists in other Pb films. The other reason is that other Pb films show similar STS spectra, indicating they have analogous band structures. More interestingly, the anisotropy of the m-band of a Pb film is smaller than for the band of the bulk, the reason for which needs more detailed studies. We can explain very strong thickness-dependent physical properties observed in Pb thin films [5–17] in terms of the 1-D-like DOS singularity developing from the 2-D band bending: it is simply because the electronic structure near  $E_F$  is now dominated by the singularity. Although we have only studied 23 and 24 ML Pb films, we know where the VHS of other Pb films is from previous STS measurements [16]. For example, the top of the m-shaped band of the 23 ML Pb film crosses the  $E_F$ , and the DOS at  $E_F$  will be markedly enhanced. This explains the defines the peculiar properties of the film with this thickness: for instance, its higher superconducting transition temperature ( $T_c$ ) [5] and Kondo temperature [16] than the 24 ML film. It should be noted that a 23 ML with an Au cap layer has a lower  $T_c$  [5], indicating that the Au cap layer influences the QWS by changing the phase shift of the interface of Pb films. In other 2-D systems like Ag thin films, however, band bending does not take place when the QWSs cross the Fermi level. Without the presence of such a singularity, enhancement of DOS near  $E_F$  due to the quantum confinement cannot be as significant as that in Pb thin films. The quantum size effects in the systems will quickly fade away with increasing film thickness [3, 4], as expected.

## 4. Conclusions

We have studied the electronic structure of Pb films in detail. The QSE and the nature of the bands of bulk Pb result in the distinctive VHS in the electron DOS. On the other hand, the binding energy of the VHS can be modulated by the QSE. As a result, the VHS induces a strong oscillation in properties even in thicker Pb films. If the VHS can cross  $E_F$  in a thinner film, the DOS at  $E_F$  will become more dominant. The tunable VHS gives new method for the study of strong correlation, such as Kondo effect and superconductivity, and other striking properties induced by the confinement of large number of electronic states.

## Acknowledgements

The work was supported by the National Natural Science Foundation of China (NSFC) and The Ministry of Science and Technology of People's Republic of China (MOST).

**Open Access:** This article is distributed under the terms of the Creative Commons Attribution Noncommercial License which permits any noncommercial use, distribution, and reproduction in any medium, provided the original author(s) and source are credited.

## References

- [1] Milun, M.; Pervan, P.; Woodruff, D. P. Quantum well structures in thin metal films: Simple model physics in reality? *Rep. Prog. Phys.* **2002**, *65*, 99–141.
- [2] Jalochofski, M.; Bauer, E. Resistance oscillations and crossover in ultrathin gold films. *Phys. Rev. B* **1988**, *37*, 8622–8626.
- [3] Luh, D. A.; Miller, T.; Paggel, J. J.; Chou, M. Y.; Chiang, T. C. Quantum electronic stability of atomically uniform films. *Science* **2001**, *292*, 1131–1133.
- [4] Paggel, J. J.; Wei, C. M.; Chou, M. Y.; Luh, D. A.; Miller, T.; Chiang, T. C. Atomic-layer-resolved quantum oscillations in the work function: Theory and experiment for Ag/Fe(100). *Phys. Rev. B* **2002**, *66*, 233403.
- [5] Guo, Y.; Zhang, Y. F.; Bao, X. Y.; Han, T. Z.; Tang, Z.; Zhang, L. X.; Zhu, W. G.; Wang, E. G.; Niu, Q.; Qiu, Z. Q.; Jia, J. F.; Zhao, Z. X.; Xue, Q. K. Superconductivity modulated by quantum size effects. *Science* **2004**, *306*, 1915–1917.
- [6] Özer, M. M.; Thompson, J. R.; Weitering, H. H. Hard superconductivity of a soft metal in the quantum regime. *Nat. Phys.* **2006**, *2*, 173–176.
- [7] Eom, D.; Qin, S.; Chou, M. -Y.; Shih, C. K. Persistent superconductivity in ultrathin Pb films: A scanning tunneling spectroscopy study. *Phys. Rev. Lett.* **2006**, *96*, 027005.
- [8] Nishio, T.; Ono, M.; Eguchi, T.; Sakata, H.; Hasegawa, Y. Superconductivity of nanometer-size Pb islands studied by low-temperature scanning tunneling microscopy. *Appl. Phys. Lett.* **2006**, *88*, 113115.
- [9] Nishio, T.; An, T.; Miyachi, K.; Eguchi, T.; Sakata, H.; Lin, S. Z.; Hayashi, N.; Nakai, N.; Machida, M.; Hasegawa, Y. Superconducting Pb island nanostructures studied by scanning tunneling microscopy and spectroscopy. *Phys. Rev. Lett.* **2008**, *101*, 167001.
- [10] Qin, S. Y.; Kim, J.; Niu, Q.; Shih, C. -K. Superconductivity at the two-dimensional limit. *Science* **2009**, *324*, 1314–1317.
- [11] Upton, M. H.; Wei, C. M.; Chou, M. Y.; Miller, T.; Chiang, T. -C. Thermal stability and electronic structure of atomically uniform Pb films on Si(111). *Phys. Rev. Lett.* **2004**, *93*, 026802.
- [12] Zhang, Y. -F.; Tang, Z.; Han, T. -Z.; Ma, X. -C.; Jia, J. -F.; Xue, Q. -K.; Xun, K.; Wu, S. -C. Oscillatory thermal expansion of Pb thin films modulated by quantum size effects. *Appl. Phys. Lett.* **2007**, *90*, 093120.
- [13] Zhang, Y. -F.; Jia, J. -F.; Han, T. -Z.; Tang, Z.; Shen, Q. -T.; Guo, Y.; Qiu, Z. Q.; Xue, Q. -K. Band structure and oscillatory electron–phonon coupling of Pb thin films determined by atomic-layer-resolved quantum-well states. *Phys. Rev. Lett.* **2005**, *95*, 096802.
- [14] Qi, Y.; Ma, X. C.; Jiang, P.; Ji, S. H.; Fu, Y. S.; Jia, J. -F.; Xue, Q. -K.; Zhang S. B. Atomic-layer-resolved local work functions of Pb thin films and their dependence on quantum well states. *Appl. Phys. Lett.* **2007**, *90*, 013109.
- [15] Ma, X. C.; Jiang, P.; Qi, Y.; Jia, J. F.; Yang, Y.; Duan, W. H.; Li, W. -X.; Bao, X. H.; Zhang, S. B.; Xue, Q. -K. Experimental observation of quantum oscillation of surface chemical reactivities. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 9204–9208.
- [16] Fu, Y. -S.; Ji, S. -H.; Chen, X.; Ma, X. -C.; Wu, R.; Wang, C. -C.; Duan, W. -H.; Qiu, X. -H.; Sun, B.; Zhang, P.; Jia, J. -F.; Xue, Q. -K. Manipulating the Kondo resonance through quantum size effects. *Phys. Rev. Lett.* **2007**, *99*, 256601.
- [17] Jia, J. -F.; Li, S. -C.; Zhang Y. -F.; Xue, Q. -K. Quantum size effects induced novel properties in two-dimensional electronic systems: Pb thin films on Si(111). *J. Phys. Soc. Jpn.* **2007**, *76*, 082001.
- [18] Wei, C. M.; Chou, M. Y. Theory of quantum size effects in thin Pb(111) films. *Phys. Rev. B* **2002**, *66*, 233408.



- [19] Shanenko, A. A.; Croitoru, M. D.; Peeters, F. M. Oscillations of the superconducting temperature induced by quantum well states in thin metallic films: Numerical solution of the Bogoliubov–de Gennes equations. *Phys. Rev. B* **2007**, *75*, 014519.
- [20] Zhang, Y. -F.; Jia, J. -F.; Tang, Z.; Han, T. -Z.; Ma, X. -C.; Xue, Q. -K. Growth, stability and morphology evolution of Pb films on Si(111) prepared at low temperature. *Surf. Sci.* **2005**, *596*, L331–L338.
- [21] Tang, S. -J.; Basile, L.; Miller, T.; Chiang, T. -C. Breakup of quasiparticles in thin-film quantum wells. *Phys. Rev. Lett.* **2004**, *93*, 216804.
- [22] Wu, J.; Choi, J.; Krupin, O.; Rotenberg, E.; Wu, Y. Z.; Qiu, Z. Q. Retrieving the energy band of Cu thin films using quantum well states. *J. Phys.: Condens. Matter* **2008**, *20*, 035213.
- [23] Upton, M. H.; Miller, T.; Chiang, T. -C. Unusual band dispersion in Pb films on Si(111). *Phys. Rev. B* **2005**, *71*, 033403.
- [24] Dil, J. H.; Kim, J. W.; Kampen, Th.; Horn, K.; Ettema, A. R. H. F. Electron localization in metallic quantum wells: Pb versus In on Si(111). *Phys. Rev. B* **2006**, *73*, 161308.
- [25] Miyata, N.; Horikoshi, K.; Hirahara, T.; Hasegawa, S.; Wei, C. M.; Matsuda, I. Electronic transport properties of quantum-well states in ultrathin Pb (111) films. *Phys. Rev. B* **2008**, *78*, 245405.
- [26] Anderson, J. R.; Gold, A. V. Fermi surface, pseudopotential coefficients, and spin–orbit coupling in lead. *Phys. Rev.* **1965**, *139*, A1459–A1481.
- [27] Van Hove, L. The occurrence of singularities in the elastic frequency distribution of a crystal. *Phys. Rev.* **1953**, *85*, 1189–1193.
- [28] Yu, P. Y.; Cardona, M. *Fundamentals of Semiconductors: Physics and Material Properties*; Springer Press: New York, 2003.
- [29] Kim, P.; Odom, T. W.; Huang, J. -L.; Lieber, C. M. Electronic density of states of atomically resolved single-walled carbon nanotubes: Van Hove singularities and end states. *Phys. Rev. Lett.* **1999**, *82*, 1225–1228.

