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2007 J. Phys.: Condens. Matter 19 136005

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# A study of the surface structure of deposited Au on Pb film

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Received 20 November 2006, in final form 21 February 2007

Published 13 March 2007

Online at [stacks.iop.org/JPhysCM/19/136005](http://stacks.iop.org/JPhysCM/19/136005)

## Abstract

Using low-temperature scanning tunnelling microscopy/scanning tunnelling spectroscopy and *in situ* reflection high-energy electron diffraction, the surface structure of deposited Au on Pb film was investigated. We observed two types of Moiré patterns, the first is formed by Au<sub>2</sub>Pb with Pb(111)  $\sqrt{3} \times \sqrt{3}$  reconstruction (Pb- $\sqrt{3}$ ) with an average period of 2.4 nm; the second is formed by AuPb<sub>2</sub> with a Pb- $\sqrt{3}$  layer with an average period of 5.8 nm. Such a surface structure changes the boundary condition of electrons confined in the Pb film. Moreover, using the structural model proposed, it consumes three monolayers (3 ML) of Pb and reduces the film thickness. These results explain well the phase shift in the oscillation of physical properties of the Pb film, which strongly depends on film thickness by the quantum size effect.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The Pb film has been studied extensively as an ideal system of quantum well states (QWSs) [1–5]. The studies demonstrate a unique bilayer oscillation of the electronic density of states (DOS) near the Fermi level ( $E_f$ ) with respect to the film thickness [3]. Many physical properties of Pb film, e.g. the local work function [6] and thermo stability [7], which depend on the DOS, also exhibit oscillatory behaviour. In particular, recent studies of the superconductivity of Pb film, such as the superconducting transition temperature ( $T_c$ ) [8] and the upper critical field [9], have attracted great interest. According to the Bardeen–Cooper–Schrieffer (BCS) theory, the  $T_c$  of Pb film depends exponentially on the DOS at the  $E_f$ , and should oscillate with a period of 2 ML. In this study [8], Au was deposited on Pb film to avoid oxidation before taking it out of the vacuum for *ex situ* measurement of  $T_c$ . As pointed out

in [8], coating Pb with Au could significantly shift the energy positions of the QWSs in the Pb films, and result in the inconsistency of oscillations between  $T_c$  and DOS that was measured *in situ*. However, more recently, Eon *et al* [10] suggested that the inconsistency was most likely due to the proximity effect of the Au overlayer. Obviously, a detailed understanding of the structure of deposited Au on Pb film is needed to clarify this issue.

In this paper, we report a study of the surface structure of Au on Pb film by low-temperature scanning tunnelling microscopy (STM), scanning tunnelling spectroscopy (STS) and reflection high-energy electron diffraction (RHEED). We found two types of Moiré patterns on the surface formed by the intermixing of Au and Pb, suggesting that 3 ML of Pb film is consumed. These results demonstrate quantitatively that the alternation of the  $T_c$  oscillation is the result of a change in the boundary condition and film thickness when Au is deposited.

## 2. Experiment

A Unisoku ultrahigh-vacuum low-temperature STM-MBE (molecular beam epitaxy) system was employed in the experiment. The MBE chamber is equipped with standard instruments for sample preparation and analysis with a background pressure better than  $1 \times 10^{-10}$  Torr. The STM system can be operated in the temperature range between 2.2 K and room temperature. The Pb films were grown at 90 K with a flux rate of  $0.5 \text{ ML min}^{-1}$  on Si(111) substrate, which was cleaned by flashing to  $1200^\circ\text{C}$  several times after 8 h of degassing at  $400^\circ\text{C}$ . After deposition, the sample was annealed at room temperature for 3 h. This procedure results in atomically smooth film [11]. Au was deposited on Pb film at room temperature with a rate of  $0.8 \text{ ML min}^{-1}$ . RHEED was used to monitor the Au growth. Then the sample was transferred *in situ* to the STM chamber and measurement was performed at 4.2 K.

The STM system works in constant-current mode with a tungsten tip. When measuring the DOS of Pb film by STS, the tip was fixed on a preconcerted point and the feedback loop was opened, then a modulating signal of 20 meV at 1 kHz was added to the sample bias, which ramped from  $-1.5$  to  $1.5$  V. A lock-in technique was used to collect the signal of the tunnelling current variation,  $\Delta I$ .

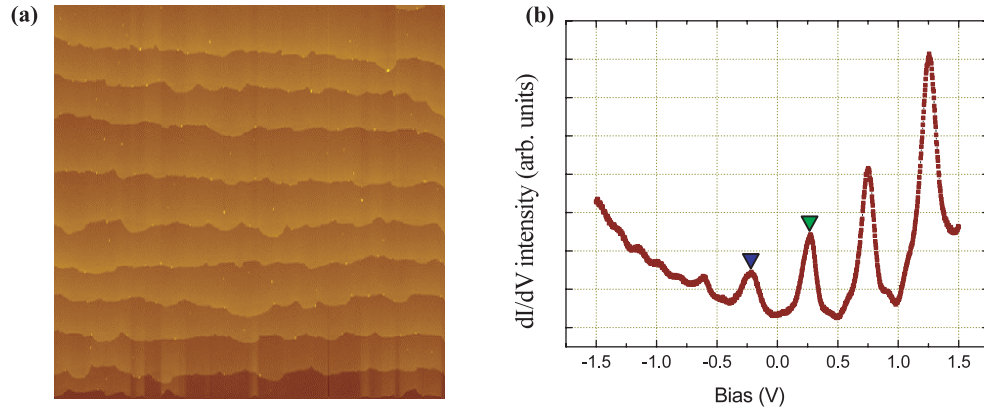
## 3. Results

Presented in figure 1(a) is an STM image of Pb film grown on a stepped Si(111) substrate. A layer-by-layer growth mode was achieved by first depositing one wetting layer on a Si(111)  $7 \times 7$  surface to relieve the strain caused by lattice mismatch between lead and silicon. The thickness of the film was determined by STS. The  $dI/dV$  curve shown in figure 1(b) exhibits several peaks, representing quantum well states formed by electrons vertically confined in the Pb film. The film thickness  $H$  is related to the energy gap  $\Delta$  [12]:

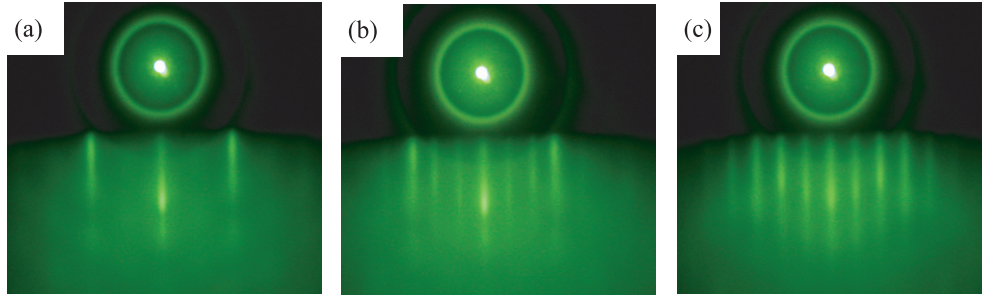
$$\Delta = \pi \hbar v_F / H \quad (1)$$

where  $\Delta$  is the difference between the highest occupied QWS and the the lowest unoccupied QWS, marked by the two triangles in figure 1(b), and  $v_F$  is the Fermi velocity of an electron. Then the film thickness was calculated to be 25 ML, including one wetting layer.

In figure 2, RHEED patterns are shown for clean Pb film, and films covered by 0.8 and 2 ML of Au. With increasing Au coverage, new fractional  $3 \times$  streaks appear at 0.8 ML and become intense and sharp at 2 ML. There is no further change in the patterns for Au coverage up to 5 ML. The sample with 2 ML Au was further investigated by STM, as shown in figure 3(a). Two types of superstructures are evident, with average periodicity of 2.4 nm for type I and 5.8 nm for type II, based on a statistical analysis of 20 STM images. It is also determined that



**Figure 1.** (a) The STM image of Pb film on Si(111) substrate taken at sample bias  $-3$  V and tunnelling current  $0.1$  nA. (b)  $dI/dV$  curve on the film, indicating the film thickness corresponding to 25 ML. The Fermi level is at  $0$  V. Triangles mark the highest occupied QWS in negative bias and the lowest unoccupied QWS in positive bias.



**Figure 2.** RHEED patterns taken along the  $[11\bar{2}]$  direction at  $10$  keV: (a) Pb film, and with (b)  $0.8$  ML, and (c)  $2$  ML of Au.

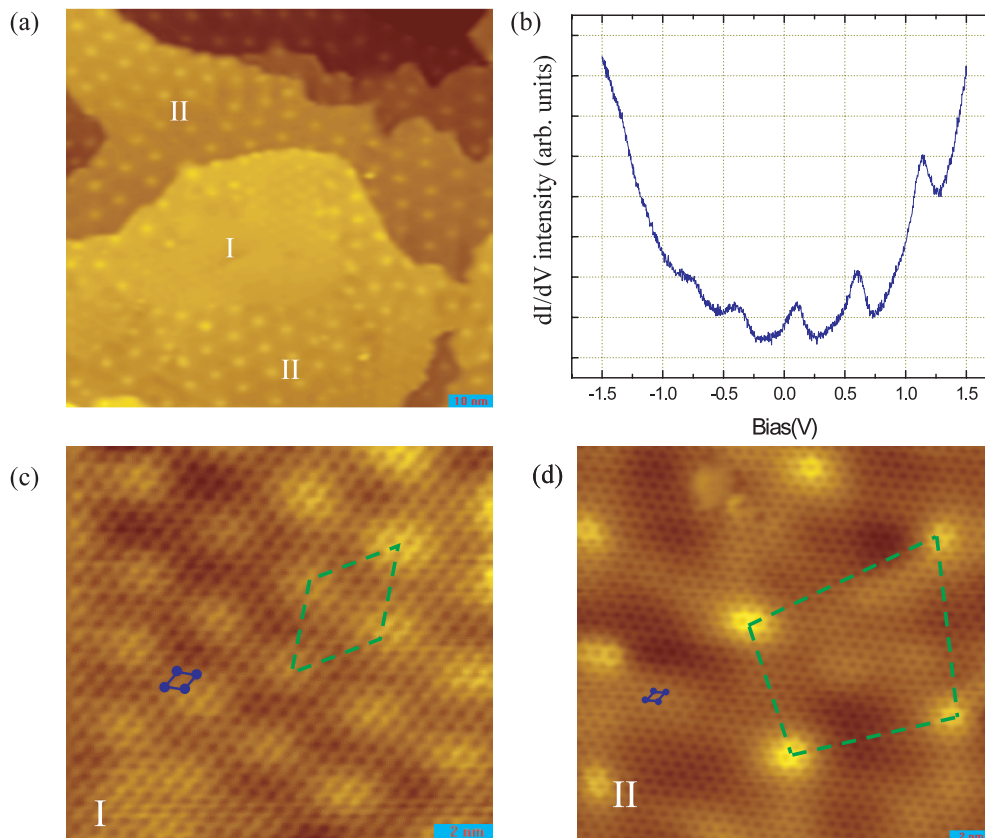
type II occupies more than five times the surface region compared with type I, which indicates that type II structure may have a lower formation energy.

The same surface was also investigated by STS. A sample  $dI/dV$  is presented in figure 3(b), which is taken on a type I region. Similar QWSs features are observed as on Pb film, but with a reduced peak amplitude and shifted peak positions. The shift and reduction vary at different locations on this surface. According to the Bohr–Sommerfeld quantization rule [13],

$$\phi_B + \phi_C + 2kH = 2\pi n \quad (2)$$

where  $\phi_B$  is the phase change of electrons at the surface and  $\phi_C$  is that of electrons at the interface between the film and the substrate. Compared with the clean surface, the reflectional phase  $\phi_B$  is obviously different for an Au-covered Pb surface, which results in the changes in the QWSs energy. Consequently, the Pb film thickness cannot be deduced easily using formula (1) any more without a detailed knowledge of the surface structure after Au deposition.

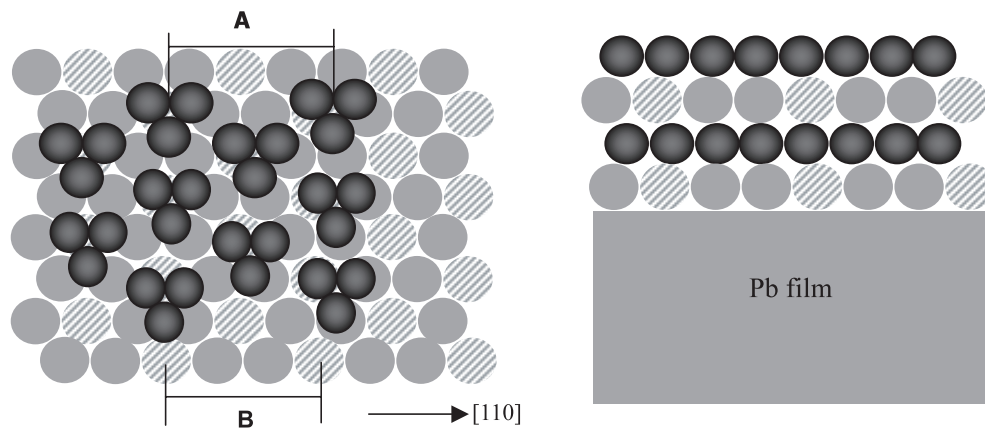
Atomic resolved STM images were taken on regions I and II, as shown in figures 3(c) and (d), respectively. On the superstructures marked with quadrilaterals there is another periodicity, indicated by the unit cell outlined. The dimensions of the unit cells are  $6$  Å, both in figures 3(c) and (d), which is consistent with the  $\text{Pb}\sqrt{3} \times \sqrt{3}$  ( $\text{Pb}-\sqrt{3}$ ) reconstruction. On



**Figure 3.** (a) STM image of the Au–Pb surface. Two types of superstructures, I and II, are found with average periods of 2.4 and 5.8 nm respectively, which are marked in (c) and (d) with quadrangles (dashed). (b)  $dI/dV$  curve on the type I area of the Au–Pb surface. (c) and (d) are the atomic resolution on type I and type II with a period of 6 Å in the marked unit cell (solid).

both regions, the  $\text{Pb}-\sqrt{3}$  layer covers the surface uniformly, and is perfect and uninterrupted even at the boundaries between the two regions, which is consistent with the clear  $3\times$  pattern observed in RHEED. These results are in agreement with an early report that a pure monolayer Pb layer is on top of the surface when Au is deposited on Pb crystal [14]. Just as the  $\text{Si}(111)-(\sqrt{3}\times\sqrt{3})\text{Ag}$  surface behaved [15], we believed that this 1 ML Pb layer takes on a  $\sqrt{3}\times\sqrt{3}$  honeycomb structure by forming trimers to achieve the lowest surface energy.

We attribute the superstructures to be Moiré patterns formed between the top  $\text{Pb}-\sqrt{3}$  layer and the underlying Au–Pb alloy layers. A Moiré pattern has been studied before, especially on graphite, and is believed to form as two different periodic lattices with close lattice distance packing together or rotating around each other [16]. The typical period of the Moiré pattern is several nanometers to tens of nanometers. In our case, two periodicities were observed, suggesting different alloy compositions. The Au–Pb phase diagram shows that the two types of alloys,  $\text{AuPb}_2$  and  $\text{Au}_2\text{Pb}$ , are stable for temperatures between 0 and 300 K [17].  $\text{AuPb}_2$  is more stable than  $\text{Au}_2\text{Pb}$  at room temperature because of the lower enthalpy of formation [18]. Therefore, we propose that  $\text{AuPb}_2$  contributes to the formation of the dominant phase, type II, and  $\text{Au}_2\text{Pb}$  contributes to type I.



**Figure 4.** (a) Structural model for the formation of Moiré patterns. The A layer is the  $\text{Pb-}\sqrt{3}$  honeycomb structure on the top layer (black balls). The B layer is the Au-Pb alloy,  $\text{Au}_2\text{Pb}$  or  $\text{AuPb}_2$  (grey balls and diagonal stripe balls with ratio 2:1). (b) The scheme of the stacking structure of Au-Pb.

Based on this supposition, the Moiré patterns observed in the STM images can be explained, as shown in the structure model presented in figure 4(a). The upper layer lattice A is the  $\text{Pb-}\sqrt{3}$  layer, with a lattice constant  $A = 10.5 \text{ \AA}$  along the  $[110]$  direction, and the underlying layer lattice B is the alloy,  $\text{Au}_2\text{Pb}$  or  $\text{AuPb}_2$ , with a unit cell lattice of  $9.28$  or  $9.88 \text{ \AA}$ , respectively<sup>3</sup>. When the two lattices pack together and meet at  $nA = (n + 1)B$ , a bright spot will occur. The periodicities were calculated to be  $2.6 \text{ nm}$  for type I and  $5.6 \text{ nm}$  for type II, which agree very well with our STM observation.

The previous investigation by LEED-AES has shown that the vertical structure of Au-Pb  $[111]$  is very complicated [14], and can be described by  $\text{Pb/L2 (L2 = AuPb}_2\text{)/Pb/L2/Pb} \dots$  rather than a simple  $\text{Pb/L2/Pb} \dots$  structure. As a surface study technique, STM cannot offer us any information more than the top layers in this study, but it is likely that a double-stacked structure is also formed in our study, as shown in figure 4(b), since similar sample preparation is involved in this study. Furthermore, our results also indicate that the L2 layer contains less than  $0.2 \text{ ML}$  of  $\text{Au}_2\text{Pb}$ .

We can also estimate that about  $3 \text{ ML}$  of Pb is consumed in the intermixed structure, including  $2 \text{ ML}$  of pure Pb, and about  $1 \text{ ML}$  in Au-Pb alloys. Therefore, there is a  $\pi$  shift in the  $T_c$  oscillation, as exhibited in [8], since the oscillation depends strongly on the film thickness [19]. Then the influence of depositing Au on Pb film is clearly understood: the Au can be used as protection for the Pb film when taken out of vacuum for *ex situ* measurements;. However, the Pb film is only perfectly preserved under an Au-Pb cap layer; a  $3 \text{ ML}$  deduction should be taken into account when relating the oscillation of physical properties to the DOS oscillation.

But there is still an open question for where the rest of the  $1 \text{ ML}$  of Au might be, because only about  $1 \text{ ML}$  of Au is used to form the double-stacked structure at the surface. Whether it ends up at the Pb-Si interface because of its smaller atom size and larger surface energy or it assembles into large clusters out of the scanning range, further studies are needed to clarify these possibilities.

<sup>3</sup> The lattice constants of alloys are calculated by assuming an hcp structure for simplicity. For  $\text{Au}_2\text{Pb}$ , the unit cell lattice is calculated from  $(2 \times R_{\text{Au}} + R_{\text{Pb}})$  with  $R_{\text{Au}} 2.88 \text{ \AA}$  and  $R_{\text{Pb}} 3.5 \text{ \AA}$ , and for  $\text{AuPb}_2$ ,  $(2 \times R_{\text{Pb}} + R_{\text{Au}})$  is performed.



#### 4. Conclusion

This study provides evidence of intermixing at an Au–Pb surface. We find that the surface structure comprises Moiré patterns formed between a layer of  $\text{Pb}\sqrt{3} \times \sqrt{3}$  reconstructed and  $\text{Au}_2\text{Pb}$  or  $\text{AuPb}_2$ . Based on the double-stacked structure model proposed, a 3 ML Pb film is consumed in the intermixing layers. A change by an odd number of layers will greatly affect some physical properties of the Pb film, which shows bilayer oscillation. Also, this influence has been observed in the  $T_c$  measurement as a  $\pi$  phase shift before and after Au deposition.

#### References

- [1] Czoschke P, Hong H, Basile L and Chiang T C 2004 *Phys. Rev. Lett.* **93** 0361031
- [2] Su W B, Chang S H, Jian W B, Chang C S, Chen L J and Tsong T T 2001 *Phys. Rev. Lett.* **86** 5116
- [3] Mans A, Dil J H, Ettema A R H F and Weitering H H 2002 *Phys. Rev. B* **66** 1954101
- [4] Menzel A, Kammler M, Conrad E H, Yeh V, Hupalo M and Tringides M C 2003 *Phys. Rev. B* **67** 165314
- [5] Hong H, Wei C M, Chou M Y, Wu Z, Basile L, Chen H, Holt M and Chiang T C 2003 *Phys. Rev. Lett.* **90** 0761041
- [6] Qi Y, Ma X, Jiang P, Ji S, Fu Y, Jia J-F, Xue Q-K and Zhang S B 2007 *Appl. Phys. Lett.* **90** 013109
- [7] Upton M H, Wei C M, Chou M Y, Miller T and Chiang T C 2004 *Phys. Rev. Lett.* **93** 0268021
- [8] Guo Y *et al* 2004 *Science* **306** 1915
- [9] Bao X-Y, Zhang Y-F, Wang Y, Jia J-F, Xue Q-K, Xie X C and Zhao Z-X 2005 *Phys. Rev. Lett.* **95** 247005
- [10] Eon D, Qiu S, Chou M Y and Shih C K 2006 *Phys. Rev. Lett.* **96** 0270051
- [11] Zhang Y-F, Jia J-F, Han T-Z, Tang Z, Shen Q-T, Guo Y, Qiu Z Q and Xue Q-K 2005 *Phys. Rev. Lett.* **95** 096802
- [12] Altfeder I B, Matveev K A and Chen D M 1997 *Phys. Rev. Lett.* **78** 2815
- [13] Milum M, Pervan P and Woodruff D P 2002 *Rep. Prog. Phys.* **65** 99
- [14] Oughaddou H, Leandre C, Aufray B, Girardeaux C, Bernardini J, Le Lay G, Biberian J P and Barrett N 2003 *Appl. Surf. Sci.* **212/213** 291
- [15] Porter T L, Chang C S and Tsong I S 1988 *Phys. Rev. Lett.* **60** 1739
- [16] Sun H L, Shen Q T, Jia J F, Zhang Q Z and Xue Q K 2003 *Surf. Sci.* **542** 94
- [17] Hassam S and Bahari Z 2005 *J. Alloys Compounds* **392** 120
- [18] Bouhajib A, Nadiri A, Yacoubi A, Bros H and Castanet R 1999 *J. Alloys Compounds* **282** 149
- [19] Chiang T C 2000 *Surf. Sci. Rep.* **39** 181