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Effects of electronic confinement and substrate on the low-temperature growth of Pb islands on Si(1 0 0)-2 × 1 surfaces

C.C. Hsu [a,b], W.H. Lin [a,c], Y.S. Ou [a], W.B. Su [a], C.S. Chang [a,*], C.I. Wu [b], Tien T. Tsong [a]

[a] Institute of Physics, Academia Sinica, Taipei 115, Taiwan, ROC
[b] Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 106, Taiwan, ROC
[c] Institute of Electrophysics, National Chiao Tung University, Hsinchu 300, Taiwan, ROC

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ABSTRACT

The growth of Pb films on the Si(1 0 0)-2 × 1 surface has been investigated at low temperature using scanning tunneling microscopy. Although the orientation of the substrate is (1 0 0), flat-top Pb islands with (1 1 1) surface can be observed. The island thickness is confined within four to nine atomic layers at low coverage. Among these islands, those with a thickness of six layers are most abundant. Quantum-well states in Pb(1 1 1) islands of different thickness are acquired by scanning tunneling spectroscopy. They are found to be identical to those taken on the Pb(1 1 1) islands grown on the Si(1 1 1)7 × 7 surface. Besides Pb(1 1 1) islands, two additional types of Pb islands are formed: rectangular flat-top Pb(1 0 0) islands and rectangular three-dimensional (3D) Pb islands, and both their orientations rotate by 90° from a terrace to the adjacent one. This phenomenon implies that the structures of Pb(1 0 0) and 3D islands are influenced by the Si(1 0 0)-2 × 1 substrate.

1. Introduction

Metal films have a wide range of applications, not only in the IC fabrication for minimizing the chip size but also in opto-electronics. The growth of metal films with atomic-scale flatness on a semiconductor has become an important issue in nanoscience and nanotechnology in recent years. Due to the lattice mismatch and the stress existing at the metal–semiconductor interface, most of metal films are formed into three-dimensional (3D) islands on semiconductor substrates [1–3]. However, recent research in the epitaxial growth of metallic thin films has shown that atomically flat Ag films with selective heights can be formed on GaAs(1 1 0) and Si(1 1 1) surfaces [4,5]. This growth phenomenon is known as a result governed by the quantum size effect (QSE) in the metal films [6,7].

For a thin metal film on a semiconductor surface, of which thickness is comparable to the de Broglie wavelength of the electrons at the Fermi level, the electrons in the conduction band, confined between the vacuum and the metal–semiconductor interface, would form the standing-wave. This confinement produces discrete energy levels of quantum-well states (QWS). The manifestation of QWS in the films is so named the QSE. The QSE in Pb films is very distinct in comparison with other films and has been intensely investigated experimentally and theoretically in recent years in epitaxial systems of Pb/Si(1 1 1) [8–18], Pb/Cu(1 1 1) [19], Pb/Ge(1 0 0) [20], and Pb/Ge(1 1 1) [21]. Interestingly, the Pb islands or films still have the (1 1 1) orientation even though they are grown on the (1 0 0) surface which has twofold or fourfold symmetry. For example, Itoh et al. have observed that Pb(1 1 1) islands can be grown on the Si(1 0 0) substrate [22]. Therefore, one can investigate the Pb/Si(1 0 0) system to compare with the Pb/Si(1 1 1)7 × 7 system whether the substrate orientation would affect the island thickness and the corresponding QWS. In this paper, we use scanning tunneling microscopy and spectroscopy to observe the growth behavior and the electronic structure of Pb(1 1 1) island on Si(1 0 0)-2 × 1 substrate at low temperature. Our results show that the island growth is indeed governed by the quantum size effect because of the manifestation of the preferred thickness. In comparison with the Pb/Si(1 1 1)7 × 7 system, however, it is found that the distribution of the preferred thickness and the energy levels of QWS in Pb(1 1 1) islands on both substrates are almost identical. Besides Pb(1 1 1) islands, atomically flat Pb(1 0 0) islands and 3D Pb islands, having twofold symmetry, are also formed. The anisotropic structure of Si(1 0 0)-2 × 1 substrate can significantly affect the growth orientations of flat-top Pb(1 0 0) islands and 3D islands, leading to the orientation rotated by 90° from a terrace to the adjacent one. Moreover, the ratios of Pb(1 0 0) islands to the 3D islands increase when the growth temperature is lower.

2. Experiment

In our experiment, Si(1 0 0) samples were cleaned in ultra high vacuum at a base pressure of 8×10^{-11} mbar. The Si(1 0 0)-2 × 1

* Corresponding author. Tel.: +886 2 2789 6722; fax: +886 2 2651 0704.
E-mail address: jasonc@phys.sinica.edu.tw (C.S. Chang).

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reconstruction can be formed by annealing the sample to 1400 K and slowly cooling it to room temperature. Lead was evaporated *in situ* onto the surface at a low temperature of 210 K with a flux of ~0.24 ML/min. The pressure is maintained below 2×10^{-10} mbar during the deposition. *I–V* spectroscopy was used to probe the QWS and the spectra were acquired at 105 K.

3. Results and discussion

3.1. Growth mode

The growth mode and surface structures of Pb/Si(1 0 0) system at room temperature have been investigated by Itoh et al. and Li et al. [22,23]. They discovered that the growth mode is the Stranski–Krastanov type, i.e. Pb is grown into a wetting layer with a coverage of three monolayers, then 3D Pb islands start to appear. In our experiment, Pb was deposited on the Si(1 0 0) surface at ~210 K, and the changes in surface reconstruction as Pb coverage increases from 0.24 to 3.6 ML are similar to the previous studies [22,23]. When the coverage is 0.24 ML, Pb atoms form Pb dimer rows and these rows are perpendicular to the Si dimer rows. At 1.08 ML, the STM image shows that the first Pb layer is of the 2×2 structure. With increasing coverage up to 2.04 ML, the second Pb layer is formed as the 2×1 structure. When the Pb coverage reaches 2.88 ML, the $c(4 \times 4)$ reconstruction is observed, as shown in a dotted rectangle in Fig. 1a. The $c(4 \times 4)$ structure consists of two orthogonal domains in each terrace. Fig. 1b is the image of this structure in higher resolution. Besides the $c(4 \times 4)$ phase, another metastable structure marked by solid rectangle in Fig. 1a is also observed, which has not been found in the previous

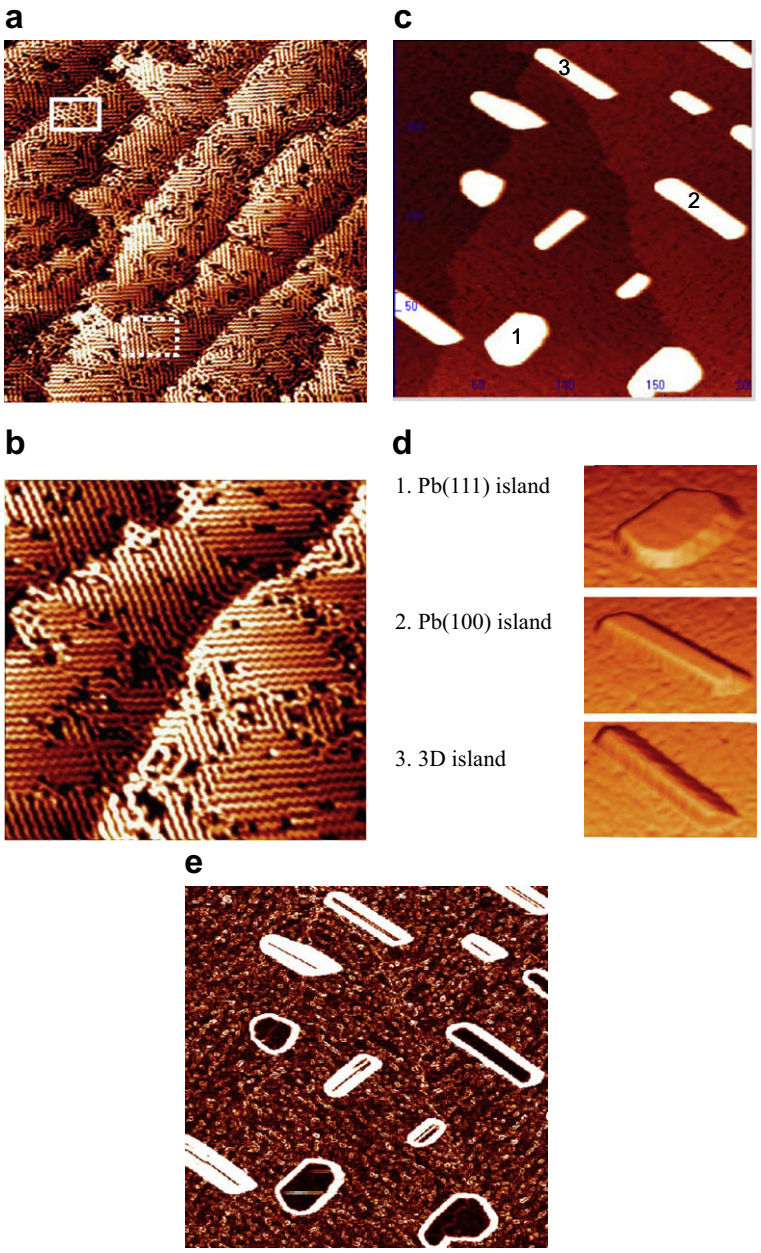

Fig. 1. (a) Double domain structure of $c(4 \times 4)$ structure (outlined by dotted line) and metastable structure (outlined by solid line) in the third layer at 2.88 ML. Scan area, 100×100 nm^2; sample bias, −2 V, tunneling current, 0.2 nA. (b) STM image of $c(4 \times 4)$ structure in higher resolution (50×50 nm^2). (c) STM image (300×300 nm^2) of three types of Pb islands at 4.32 ML. (d) 3D images of the Pb(1 1 1) island, Pb(1 0 0) island and 3D island. (e) Edge differential image shows the top of the Pb(1 1 1) and Pb(1 0 0) island is flatter than the wetting layer.

studies at room temperature. When the Pb coverage exceeds 3 ML, Pb islands start to appear on the wetting layer. Fig. 1c shows the growth of islands at coverage of 4.32 ML. It can be seen that the islands can be formed with either rectangular or hexangular shape. The 3D images of islands in Fig. 1d further exhibit that islands can be divided into three categories. The first type is the flat-top hexangular Pb(1 1 1) island. The second type is the flat-top Pb island with rectangular shape indicating that its top surface is (1 0 0) orientation. The third type is the 3D Pb islands with rectangular base. Fig. 1e is the edge differential image, showing that the top surfaces of the Pb(1 1 1) and Pb(1 0 0) island is flatter than the wetting layer.

3.2. Pb(1 1 1) island

In this section, we focus on the properties of Pb(1 1 1) islands. Fig. 2 is a statistical result of the distribution ratio as a function of island thickness for two different coverages at 210 K. The thickness of islands is confined within four to nine atomic layers. Since four layers is the minimum thickness we have observed, it represents the threshold thickness for the formation of Pb islands. Islands with a thickness of six layers have the highest ratio, indicating that six layers are the magic thickness for the growth of Pb islands. We analyzed the average thickness and the area of islands, and found that the average thickness increases only ~9%, even though the coverage (above the wetting layer) increases by a factor of 2. However, the average area of islands increases by a factor 1.7, which denotes that the growth of islands prefers the lateral direction. Pb islands can be of six kinds of preferred thickness and reveal lateral growth behavior, indicating that their formation is driven by the QSE and the QWS should exist in islands.

To explore the existence of QWS in the Pb islands, we measure *I*–*V* spectra of islands with different thickness. Fig. 3a shows *I*–*V* spectra measured on 4-, 5-layer thick islands and the wetting layer. By differentiating the tunneling current with respect to the sample bias, the density of states of Pb islands can be obtained. In order to make the signal more distinct, the d*I*/d*V*–*V* curves of these islands are further divided by *I*/*V* to normalize the spectra. Fig. 3b shows the normalized spectra of the islands of different thickness. The number *N* on the right hand side represents the number of layers of Pb islands above the wetting layer. We can observe two peaks around the Fermi level in each spectrum, which are the well-known QWS. The down-pointing and up-pointing arrows mark

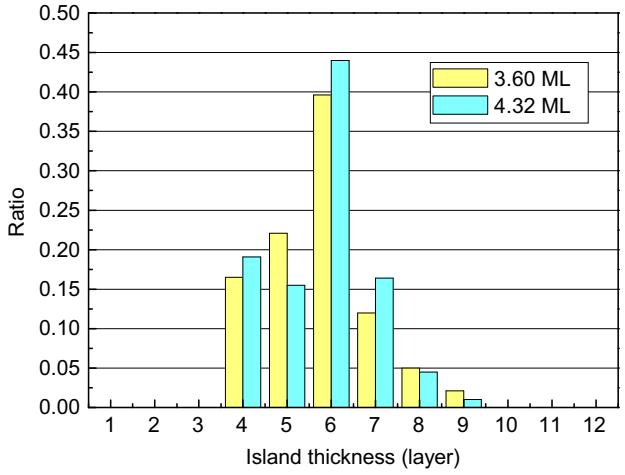

Fig. 2. The distribution ratios as a function of island thickness at two different coverages. The thickness of islands is confined within the range of four to nine atomic layers and the six-layer-thick island has the highest ratio.

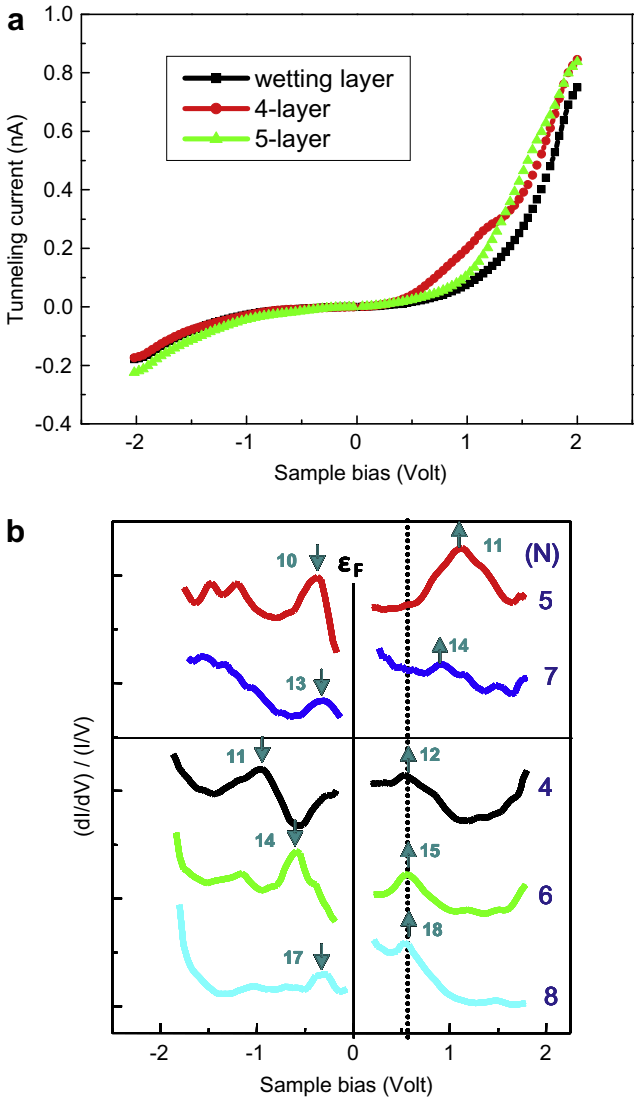

Fig. 3. (a) *I*–*V* spectra measured on four- ad five-layer thick islands and the wetting layer. (b) The quantum states in d*I*/d*V*/*I*/*V* spectra around the Fermi level for different thicknesses of islands. The energy levels and the quantum numbers of quantized states are marked by the arrows and the numbers. The down-pointing and up-pointing arrows mark the QWS in empty states and filled states.

the energy levels of quantum-well states in the empty state and the filled state, respectively.

While the positions of some peaks are changed with the thickness, it can be seen in Fig. 3b that a peak located at 0.56 eV above Fermi level, indicated by a dashed line, is clearly independent of the thickness in the spectra of $N = 4$, 6, and 8. Previous studies [11,12] on Pb/Si(1 1 1)7 × 7 system have found this peak at the same energy and have identified the wave vector k of this specific QWS to be $3\pi/2d_0$, where d_0 is the interlayer spacing along (1 1 1) direction. The existence of this peak implies that the finite square well of the islands can be approximated by an infinite square well with a width of $W = Md$, where M has to be an even integer. Since the number N of this peak is even, M could be equal to N, $(N + 2)$, $(N + 4)$, and so on. The quantization condition for the infinite potential well is

$$kMd = n\pi \tag{1}$$

where n is the quantum number. Owing to the fact that the wave vector of the thickness-independent peak is known, we can assign

the quantum number of each peak. First, we assume $M = N$, $(N + 2)$, and $(N + 4)$, and then substitute these equations into Eq. (1) to obtain three sets of quantum numbers, respectively. Second, in order to examine which set is valid, the energy separation ΔE between adjacent states was calculated by using the equation

$$\Delta E = \frac{n^2\pi^2\hbar^2}{2m^*W^2} - \frac{(n-1)^2\pi^2\hbar^2}{2m^*W^2} = \frac{(2n-1)\pi^2\hbar^2}{2m^*W^2} \quad (2)$$

where m^* is the effective mass in the [1 1 1] direction, which is $1.14m_0$. Fig. 4a shows the comparison between the experimental and theoretical results, and we find that only the case of $M = N + 4$ agree with the experimental results. Finally, since the relationship between M and N is determined, the right quantum number of each QWS can be assigned, as marked by numbers near peaks in Fig. 3b. Previous studies and our measurement show that the wetting is about 3 ML. Therefore, the width of the quantum well in the Pb island would be $N + 3$, one layer less than aforementioned $M = N + 4$. The additional one layer originates from the quantum well being finite, and the electron can penetrate into the barriers at Pb/Si and Pb/vacuum interfaces. With assumption of the penetration depth being d/2 on both sides, they will add up to the additional layer. The penetration depth mainly depends on energy. Owing to that the observed quantum-well states are around the Fermi level and the energy separations between the quantum-well states are within the range of 2 eV, which are much smaller than the inner potential of 13.08 eV of the Pb islands [24]. Therefore, it is plausible to consider that the penetration depth is nearly not changed in the range of 2 eV and is the same for the observed quantum-well states. Fig. 4b illustrates this geometric relation and the dots indicate the layer positions. Moreover, the magic thickness including the wetting layer in this growth system is nine layers, which is the same as that of Pb/Si(1 1 1)7 × 7 system. Both systems also reveal several kinds of preferential thickness and similar energy levels of QWS. These results show that the influence of substrate symmetry is insignificant on the QSE-induced growth behavior in these two systems. According to the model of the electronic growth [6], the charge spilling is a key factor to determine the preferred thickness of the metallic films with the quantum-well states. Because of the identical magic thickness, it is plausible to infer that the situation of the charge spilling at the Pb/Si interface is similar for both orientations, and thus the barrier at Pb/Si interface for reflecting electrons is close for both substrates. This explains why energy levels of QWS in both systems are almost identical.

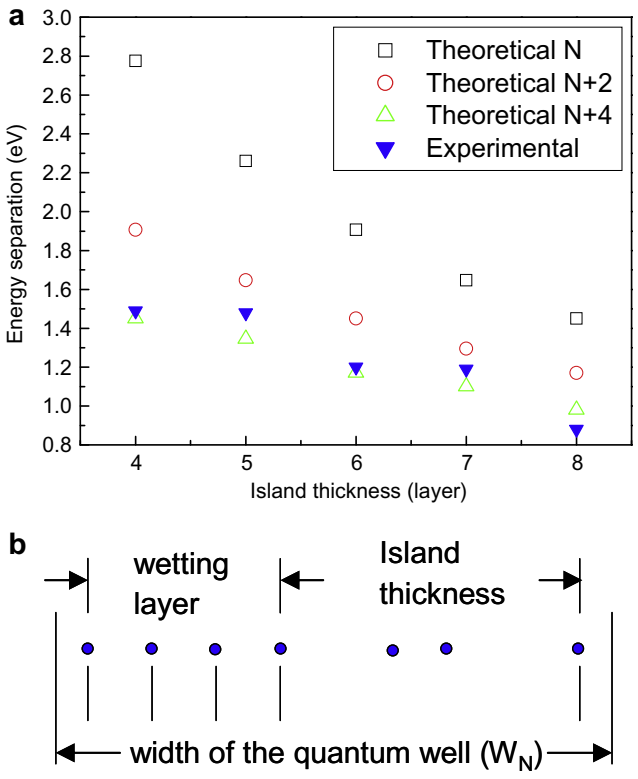

Fig. 4. (a) Comparison between the measured energy separation in Fig. 3b and the theoretical calculation. (b) A sketch to illustrate the actual width of the quantum well.

3.3. Pb(1 0 0) island and 3D island

We have shown in Fig. 1a that $c(4 \times 4)$ structure and the metastable structure coexist on the wetting layer. These two structures orient at 45° to the step edge, i.e., 45° with respect to the Si dimer rows. However, Fig. 1b emerges that Pb(1 0 0) islands and 3D

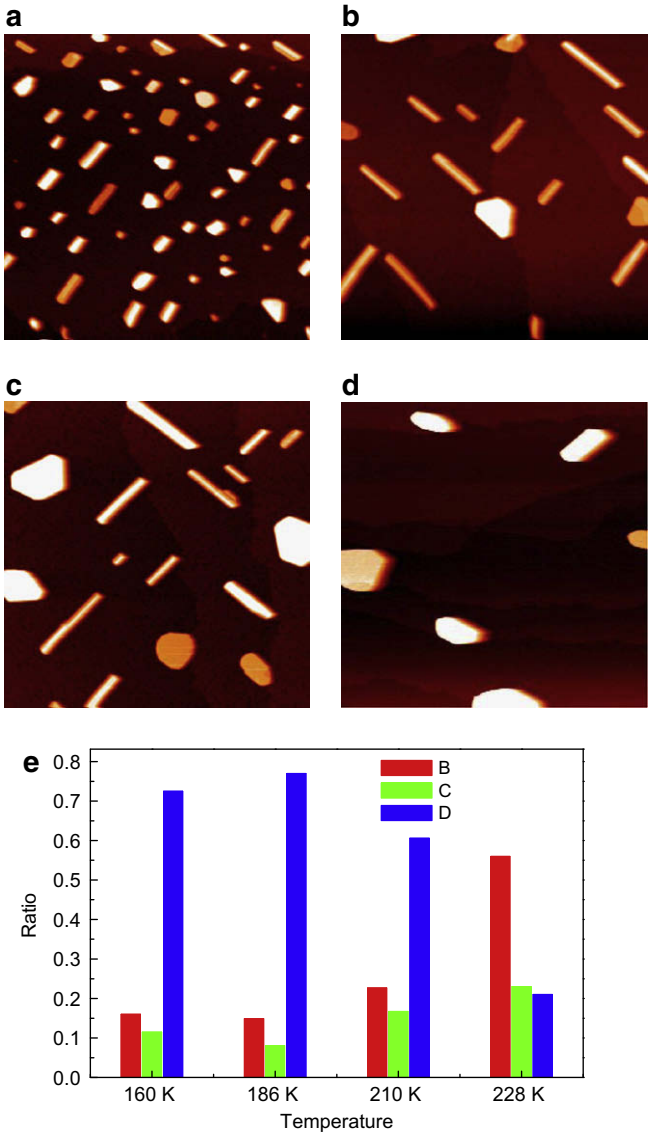

Fig. 5. STM images (300 × 300 nm^2) of Pb islands grown at: (a) 160 K, (b) 186 K, (c) 210 K, and (d) 228 K with a coverage of 4.32 ML. (e) Distribution ratio of three kinds of islands at four different temperatures. The number of 3D Pb islands decreases significantly and the number of Pb(1 1 1) island increases at 228 K, indicating that the Pb atoms prefer to nucleate Pb(1 1 1) islands over 3D Pb islands.

islands rotate by 90° from one terrace to the adjacent one. This observation implies that, unlike Pb(1 1 1) in the previous section, the 2D Pb(1 0 0) and 3D islands are influenced by the Si(1 0 0)-2 × 1 surface. According to the structure models of the Pb 2 × 1 configuration in the second layer and of the $c(4 \times 4)$Pb surface [22,23], the Pb ad-dimers in $c(4 \times 4)$ have the same orientation as the that of Si dimers under the wetting layer. Therefore, by comparing the orientations of the longer edges of the Pb(1 0 0) islands and 3D islands with Pb ad-dimers, we can know that the longer edge of these islands are parallel to the Si dimer rows.

It is interesting to note that the growth of Pb(1 0 0) island and 3D island are affected by the Si dimer rows instead of $c(4 \times 4)$ structures. Previous research shows the Si(1 1 1)-7 × 7 structure can be directly observed under the Pb islands with a STM [25], manifesting that the structure of wetting layers under the island was crystallized. Besides, previous study shows that the formation of an elongated island during MBE on Si(1 0 0)-2 × 1 surface is attributed to the preferential diffusion of adatoms along the dimer row direction [26], thus leading to the rectangular shape of Pb(1 0 0) islands and 3D islands.

3.4. Temperature effect

Fig. 5a–d shows the growth of Pb islands at four different temperatures (160 K, 186 K, 210 K, 228 K) at coverage of 4.32 ML. It can be seen that all three kinds of islands can be observed in this temperature range. Moreover, as temperature increases, the island density decreases and the island size increases, manifesting a competing process between the nucleation and the size growth. The competition arises because the mobility of Pb atoms is faster at higher temperature; the probability for an atom to attach to an existing island is higher than that to nucleate a new island. The thickness measurement reveals that the thickness of Pb(1 1 1) islands is still confined in four to nine layers at 228 K, indicating that the effect of quantum confinement sustains even when the temperature reaches 228 K.

Fig. 5e is a statistical result of the ratio distribution for three kinds of islands at four different temperatures. The 3D rectangular Pb island has the highest ratio in the temperature range of 160–210 K, indicating that the diffusion of most of Pb atoms are restricted by the 2 × 1 reconstruction of Si(1 0 0) substrate. However, the ratio of Pb(1 1 1) island rapidly increases when the temperature changes from 186 to 228 K. This can be attributed to that the (1 1 1) surface has the lowest surface energy, and thus Pb(1 1 1) island has a probability to appear even the substrate is (1 0 0) surface. The appearance of more isotropic Pb(1 1 1) islands indicates that the mobile atoms on the wetting layer can overcome the anisotropic influence of the underneath Si(1 0 0) dimer surface to form into islands with the (1 1 1) surface. Therefore, it is obvious that there is a competition among the formations of the (1 1 1) and more elongated 3D and (1 0 0) islands. In our opinion, what type of the island is formed is determined by the mobility of surface atoms in the direction across the dimer rows, and is thus dependent on the growth temperature. Therefore, the slight temperature difference shown in Fig. 5 for island distributions reflects the small difference in the diffusion barriers along and across the direction of the dimer rows.

4. Conclusion

Using the scanning tunneling microscopy, we have investigated three kinds of Pb islands on the Si(1 0 0)-2 × 1 at low temperature. When the coverage is less than 4.5 ML and the temperature range is between 160 and 228 K, flat-top Pb(1 1 1) islands are formed. The thickness of Pb(1 1 1) islands is confined within the range of four to nine layers, and the six-layer islands are the most abundant. Furthermore, with increasing coverage, Pb islands exhibits a two dimensional growth behavior. These growth characteristics indicate that the quantum size effect plays an important role in the Pb(1 1 1) island growth. Quantum-well states are also observed in the Pb(1 1 1) island. The quantum numbers can be assigned because of the manifestation of the thickness-independent state in the spectra of the islands with even-layer thickness. The spectra of Pb(1 1 1) island on Si(1 0 0)-2 × 1 reveal that the energy levels of quantum-well states are similar to those in the Pb/Si(1 1 1)-7 × 7 systems. The flat-top Pb(1 0 0) islands and 3D islands rotate by 90° from one terrace to the adjacent one. This phenomenon implies that the growth of Pb(1 0 0) and 3D islands are influenced by the Si(1 0 0)-2 × 1 substrate.

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